

# Catalytic Halogen-Exchange Fluorination of 4-Chlorobenzaldehyde to 4-Fluorobenzaldehyde, a Greener Process

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**Abstract:** The direct halogen-exchange fluorination of 4-chlorobenzaldehyde was studied under solvent-free and various diphenyl solvents conditions using spray-dried KF as a fluorinating agent. Aspects influencing the selectivity and yield of product were investigated in detail, including catalysts and solvents selection, reaction conditions optimization, and side product control. We paid more attention to issues from a perspective of industrial process, such as product separation and catalyst/solvent recycling. The reaction works efficiently with tetraphenyl phosphonium bromide as a phase transfer catalyst under solvent free conditions and in diphenyl solvents. Under the optimum reaction conditions, the yield of 4-fluorobenzaldehyde reached 90% with a selectivity of 98%.

## Introduction

Halogen-exchange (Halex) fluorination with a metal fluoride salt as a fluorine source is a convenient method to produce fluoro compounds.<sup>[1]</sup> This is a greener alternative to the classic Schiemann reaction that involves the diazotization of anilines followed by the thermal decomposition of the intermediate arenediazonium fluoroborates.<sup>[2]</sup> Because of the low stability of the intermediates, the reactions for diazotization of anilines are usually carried out in strong acid solution at low temperatures. The whole process generates large amount of harmful wastes. The Schiemann reaction is used for the production of some important chemicals for insecticides and herbicides, such as 2,6-difluorobenzonitrile and 2,4-difluoroaniline.<sup>[3]</sup>

Metal fluoride salt is a clean and easily accessible fluoride source for the halogen-exchange fluorination reaction. Due to the poor solubility of the metal fluoride salt, a polar solvent and a phase transfer catalyst are usually employed for the reaction. The phase transfer catalysts could be quaternary phosphonium salts,<sup>[4]</sup> quaternary ammonium salts,<sup>[5]</sup> crown ethers<sup>[6]</sup> and polyethylene glycols.<sup>[7]</sup> Dipolar aprotic solvents rather than protic solvents are usually used for the process on a larger scale.<sup>[3]</sup> Commonly used dipolar aprotic solvents could be dimethylsulfoxide (DMSO),<sup>[3, 5d, 8]</sup> tetramethylenesulfone (called sulfolane),<sup>[3, 8-9]</sup> N,N-dimethylformamide (DMF),<sup>[3, 5d]</sup> halobenzene,<sup>[9-10]</sup> N-methylpyrrolidone (NMP),<sup>[3, 8]</sup> nitrobenzene,<sup>[9, 11]</sup> and benzonitrile.<sup>[3, 8]</sup> However, some solvents like DMSO and sulfolane have poor thermal stability at higher reaction temperatures and side products can result from the solvents under drastic conditions. Water is environmentally friendly and is highly sought after as a media for synthesis.

Recently, there have been research works using water as a (co)solvent and/or a reactant for fluorination reactions.<sup>[12]</sup> Nucleophilic fluorinations regulated through hydrogen bonding interactions have also been reported.<sup>[13]</sup> From the viewpoint of commercial application, there are several challenges which restrict this Halex reaction as a green alternative for the traditional Schiemann reaction, including low selectivity and yield for product, less efficient product isolation/purification system, and lacking practically feasible catalyst and solvent recycling methods.

4-Fluorobenzaldehyde is an important fluorinated benzaldehyde which can be used in the synthesis of pesticides and pharmaceuticals<sup>[9-11]</sup> and other compounds such as chalcone derivatives<sup>[14]</sup> and azo dyes.<sup>[15]</sup> 4-Fluorobenzaldehyde is currently synthesized by the traditional diazotization of anilines, which is not an environment benign process. The synthesis of 4-fluorobenzaldehyde by direct halogen-exchange fluorination of 4-chlorobenzaldehyde has long been explored,<sup>[9-11, 16]</sup> as 4-chlorobenzaldehyde can be easily produced through the chlorination of 4-chlorotoluene followed by hydrolysis or through the oxidation of 4-chlorotoluene.<sup>[17]</sup> For example, nearly 80% of product yield could be achieved from halogen-exchange fluorination of 4-chlorobenzaldehyde in nitrobenzene solvent with tetraphenyl phosphonium bromide as a phase transfer catalyst.<sup>[9, 11]</sup> However, this method is not suitable for large scale production due to the difficulty of product separation. The boiling point of nitrobenzene (210 °C) is close to that (214 °C) of 4-chlorobenzaldehyde which is very challenge for the distillation process. Herein, we studied the halogen-exchange fluorination of 4-chlorobenzaldehyde from a perspective for large scale production. We paid attention not only to factors that may affect the reaction itself but also to those aspects of product isolation as well as materials recycling. The side product control related to the defluorination of the product was also studied as it is commonly observed under drastic reaction conditions.<sup>[9, 18]</sup>

## Results and Discussion

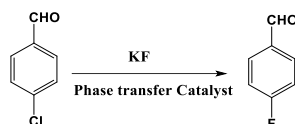
Phase transfer catalysts (PTC) play key roles in direct halogen-exchange reactions because of their ability for the solvation of the halogen sources usually in salt forms. A good phase transfer catalyst should be efficient, cheap, and stable under the reaction conditions. In the initial catalyst screening, tetraphenyl phosphonium bromide demonstrated superior

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performance in nitrobenzene solvent (Table S1). However, high catalyst loading of 10 mol% is needed to achieve high yield of 72.2%.

Other factors affecting the reaction were also studied for the tetraphenyl phosphonium bromide catalyst (Table 1). Addition of acid and base hampered the reaction significantly (Entries 2-4, Table 1). Run of the reaction under air atmosphere also led to lower selectivity, probably because of the over-oxidation of product (Entry 6, Table 1). It is noteworthy that add small amount of zinc powder into the system could increase the selectivity under both nitrogen and air atmosphere (Entries 5 & 7, Table 1), probably because zinc eliminated the oxygen in the system and hence prevented the over-oxidation of product. The effect of Zn additive would be significant when the reaction is run in large scale in air. The tolerance for water was also tested (Entries 8-10, Table 1). Add trace amount of water (e.g., 1  $\mu$ L) into the systems promoted the reaction probably because of the improved solubility of KF. However, when more water (e.g., 5  $\mu$ L) was added, the reaction became sluggish.

**Table 1.** Optimizing reaction condition (gas protection, additives) for the halogen-exchange fluorination of 4-chlorobenzaldehyde.



Entry	Additive	Conv. /%	Yield /%	Sel. /%
1	-	94.2	72.2	76.6
2	H <sub>2</sub> SO <sub>4</sub>	3.9	0.6	-
3	Amberlyst-15	18.7	8.1	-
4	CsOH	7.9	0.7	-
5	Zn 10 mg	89.3	78.0	87.3
6 <sup>[a]</sup>	-	95.1	61.2	64.3
7 <sup>[a]</sup>	Zn 10 mg	95.8	71.3	74.4
8	H <sub>2</sub> O 1 $\mu$ L	85.4	77.4	90.6
9	H <sub>2</sub> O 2 $\mu$ L	92.1	72.3	78.5
10	H <sub>2</sub> O 5 $\mu$ L	6.1	2.6	42.6

Reaction conditions: 4-chlorobenzaldehyde 5 mmol, KF 6 mmol (1.2 eq.), Ph<sub>4</sub>PBr 0.5 mmol (10 mol%), nitrobenzene 1.0 mL, 210 °C 12 h. Acid or base additive, 4 mol%. Zn powder, 10 mg. [a] The reactions were run in air instead of nitrogen gas. Conversions and product yields were determined by GC analysis using mesitylene as an internal standard.

The above results show that the halogen-exchange fluorination of 4-chlorobenzaldehyde is efficient with tetraphenyl phosphonium bromide catalyst in the 4-nitrobenzene solvent. However, challenges for high catalyst loading and product separation (distillation) are still retained. The boiling points of 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, and the nitrobenzene solvent are 181, 214 and 211 °C, respectively. Because the difference between the boiling points for 4-chlorobenzaldehyde and the nitrobenzene solvent is less than 5 °C, it would be challenging in separating and recovering of the unreacted 4-chlorobenzaldehyde from the solvent. In view of this consideration, we tried to run the reaction under solvent free conditions and explore other solvents more suitable than nitrobenzene for this reaction. The reactions under solvent free conditions work as efficient as that in nitrobenzene solvent at

small scale (Table 2). Because of the higher concentration of substrates and catalyst, over 70% product yield could still be achieved when the loading of catalyst was reduced to 5 mol% or the reaction temperature was decreased to 180 °C. When the loading of catalyst was further reduced to 2.5 mol%, the yield for product decreased to about 60%.

**Table 2.** Halogen-exchange fluorination of 4-chlorobenzaldehyde under solvent free conditions.

Entry	PTC /mol%	T /°C	t /h	Conv. /%	Yield /%
1	10	210	12	94.7	74.8
2	5	210	12	90.7	70.9
3	5	210	18	96.7	75.4
4	5	200	24	99.5	78.6
5	5	190	24	88.3	77.6
6	5	180	24	89.4	78.4
7	2.5	210	12	71.7	61.0
8	2.5	210	18	76.0	58.0

Reaction conditions: 4-chlorobenzaldehyde 5 mmol, KF 6 mmol (1.2 eq.), Ph<sub>4</sub>PBr 0.15 ~ 0.5 mmol (2.5 ~ 10 mol%). All reactions were run in nitrogen gas. Conversions and product yields were determined by GC analysis using mesitylene as an internal standard.

Thought the halogen-exchange fluorination of 4-chlorobenzaldehyde works well at small scale under solvent free conditions, the use of a suitable solvent is desirable for better mass transfer especially at large scale production. For easy separation of the product and unreacted substrate, a solvent with boiling point at least 20 °C higher than that (214 °C) of 4-chlorobenzaldehyde is preferred. Some high boiling point solvents have been explored for this reaction (Table S2). As aforementioned, protonic solvents are less adopted than aprotic ones. Diphenyl solvents have high boiling points (> 250 °C) and they are compatible with aromatic reagents. Some diphenyl solvents are therefore tested for the reaction, including diphenyl methane (Ph<sub>2</sub>CH<sub>2</sub>), diphenyl ether (Ph<sub>2</sub>O), diphenyl ketone (benzophenone, Ph<sub>2</sub>CO), and diphenyl sulfone (Ph<sub>2</sub>SO<sub>2</sub>, DPS). In the less polar Ph<sub>2</sub>CH<sub>2</sub> and Ph<sub>2</sub>O solvents, over 90% conversions and over 77% product yields could be achieved at 10 mol% of catalyst loading; when the loading of catalyst decreased to 5 mol%, the conversion and product yield decreased drastically to 40% and 30% in Ph<sub>2</sub>CH<sub>2</sub> solvent and even lower values in Ph<sub>2</sub>O solvent. In more polar Ph<sub>2</sub>CO solvent, 78.3% product yield was achieved at 10 mol% catalyst loading and 70.9% yield was achieved when catalyst loading was reduced to 5 mol%. Diphenyl sulfone (Ph<sub>2</sub>SO<sub>2</sub>) is a dipolar aprotic solvent with a boiling point up to 379 °C.<sup>[19]</sup> It was found that in Ph<sub>2</sub>SO<sub>2</sub> solvent, the reaction is more efficient than in other diphenyl solvents. With 10 mol% of catalyst loading, over 80% product yield was achieved in 6 h at 210 °C. When the loading of catalyst was 5 mol%, approximately 90% product yield (97% selectivity) was achieved in 12 h at 210 °C. Further reduction of the loading of catalyst to 2.5 mol%, the yield of product decreased to 33% (46% selectivity). To our knowledge, the result at 5 mol% of catalyst loading in this particular diphenyl sulfone solvent is among the best for the direct halogen-exchange fluorination of 4-chlorobenzaldehyde. The high boiling

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point of this solvent enables the easy separation of product and substrate by distillation.

The reaction variables such as the loading of catalyst and the reaction time have therefore been optimized for the diphenyl sulfone solvent (Table 3). The reaction rate decreased with decreasing loading of the catalyst. However, it is noteworthy that when catalyst loading was > 5 mol%, high product selectivity (> 97%) was always achieved under various conditions. At 2.5 mol% of catalyst loading, the selectivity of product was 46% at 12 h and improved to 69% at 16 h. The high selectivity achieved in diphenyl sulfone is likely related to its high polarity, stability and compatibility with the substrate and catalysts.

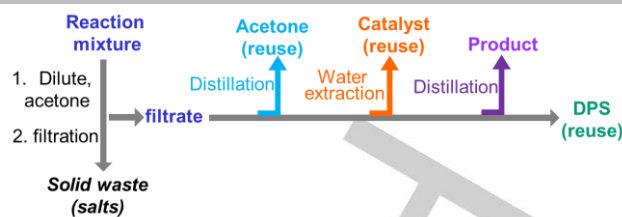
**Table 3.** Halogen-exchange fluorination of 4-chlorobenzaldehyde in diphenyl sulfone solvent.

PTC/mol%	T/°C	t/h	Conv. /%	Yield /%	Sel. /%
10	210	12	89.0	88.8	99.8
10	210	6	82.0	81.3	99.1
10	210	3	66.4	66.2	99.7
5	210	16	88.6	86.7	97.9
5	210	12	92.0	89.5	97.3
5 <sup>[a]</sup>	210	12	94.7	82.3	86.9
5	210	6	79.2	79.1	99.9
2.5	210	16	86.1	59.7	69.3
2.5	210	12	71.7	32.9	45.9

Reaction conditions: 4-chlorobenzaldehyde 5 mmol, KF 6 mmol (1.2 eq.), Ph<sub>4</sub>PBr 0.15 ~ 0.5 mmol (2.5 ~ 10 mol%), Ph<sub>2</sub>SO<sub>2</sub> solvent 1.0 mL. All reactions were run in nitrogen gas. [a] Recycled catalyst. Conversions and product yields were determined by GC analysis using mesitylene as an internal standard.

Larger scale reaction (10.5 g of 4-chlorobenzaldehyde) was performed in diphenyl sulfone solvent with the results shown in Table S3. Because of difficulty in mass transfer at larger scale reaction, intensified reaction conditions were applied, such as longer reaction time and higher reaction temperatures. At slightly higher reaction temperature (225 °C) than that (210 °C) used for small scale reaction, over 80% product yield was achieved in 24 h. With diphenyl sulfone as the high boiling point solvent, the separation of product and solvent was quite straightforward (see Supporting Information). The 4-fluorobenzaldehyde product was separated by simple distillation as a colorless liquid (6.5 g, 70% yield, Figure S1), and the diphenyl sulfone solvent was recovered as a white solid by recrystallization in acetone (14.2 g, 95% yield, Figure S2).

Defluorination of product under the drastic reaction conditions is usually observed in halogen-exchange fluorination.<sup>[18]</sup> Because the boiling points of the fluorination product and the defluorination product are very close, the purity of the product will be affected when defluorination is significant. Our research indicated that there are 0.15% of product defluorinated under solvent free conditions and 0.09% of product defluorinated in diphenyl sulfone solvent. To suppress the free radical induced defluorination reaction, 2,2'-dinitrobiphenyl was selected as radical scavenger additive.<sup>[9, 18]</sup> With about 1 mol% of 2,2'-dinitrobiphenyl added into the system, the defluorination was negligible (Table S4).



**Scheme 1.** Process diagram for product isolation and material recycling.

In Scheme 1 we illustrate the possible process for product isolation and catalyst/solvent recycling in larger scale synthesis. After the reaction, the reaction mixture was diluted with acetone/ethanol and filtrated to remove the solid salts. We found that removal of the inorganic salts at an earlier stage is beneficial for good quality of product and the recycled catalyst. Acetone or ethanol can be recycled from the filtrate after distillation. Subsequently, the Ph<sub>4</sub>PBr catalyst was recovered by water extraction and purified by re-precipitation. With up to 60 mol% of catalyst could be recovered by this water extraction method in cases with or without solvent used in the fluorination reactions. The recovered catalyst demonstrated the same catalytic activity as fresh catalyst after fine drying in vacuum (Table 3). Then, the product can be collected by distillation. The DPS solvent remained in the residue can be purified by re-crystallization from acetone. Based on our demonstrations, we assume that the current method is also applicable for the Halex synthesis of other fluorinated compounds with similar structures such as 2-fluorobenzaldehyde, which is also an important intermediate in pharmaceutical synthesis.

## Conclusion

The direct fluorination of 4-chlorobenzaldehyde was studied under solvent-free conditions and in various diphenyl solvents. Factors influencing the selectivity and yield for desired product were investigated in detail, including selection for catalysts and solvents, reaction conditions, and side product control. Tetraphenyl phosphonium bromide is the most efficient phase transfer catalyst for the process. Inert gas protection or addition of metallic zinc into the system improved the product selectivity. Under solvent free conditions with tetraphenyl phosphonium bromide as a phase transfer catalyst, 70 ~ 80% of product yield was achieved. In diphenyl sulfone solvent, the yield for 4-fluorobenzaldehyde reached 90% with a selectivity of 98%. The defluorination of the product could be suppressed by adding trace amount of 2,2'-dinitrobiphenyl. The product isolation, catalyst and solvent recycling conditions have also been successfully optimized and demonstrated the potential of current process for industrial application.

## Experimental Section

Spray dried KF was used as a fluorine source. Spray-dried KF was provided by Wanlong Chemicals. Other chemicals were purchased from Sigma-Aldrich. All solid reagents were heated under vacuum at 40 ~ 60 °C for at least 12 h. All liquid solvents used were pretreated with CaH<sub>2</sub> or 5 Å molecular sieve for 2 days. The fluorination of 4-chlorobenzaldehyde was performed in thick-wall pressure vials (8 mL). In a typical procedure, 4-chlorobenzaldehyde 5 mmol, KF 6 mmol, Ph<sub>4</sub>PBr 0.5 mmol,

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nitrobenzene 1.0 mL were charged into the thick-wall pressure vials (8 mL) and sealed under dry nitrogen gas. Contents of the vials were stirred at certain temperature (e.g., 210 °C) for 12 h. The samples containing known amount of mesitylene as an internal standard were analyzed by Agilent gas chromatography GC6890N with FID and capillary column (HP FFAP, 30 m × 0.32 mm, 0.25 μm).

## Acknowledgements

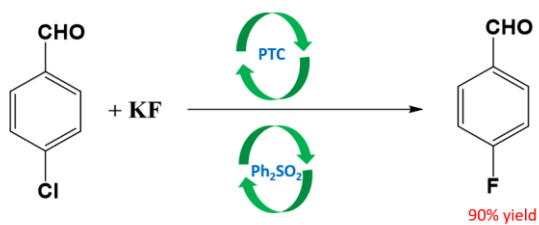
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**Keywords:** 4-Chlorobenzaldehyde • Halogen-Exchange • Fluorination • Phase Transfer Catalyst • Diphenyl Solvents

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## Entry for the Table of Contents



The direct halogen-exchange fluorination of 4-chlorobenzaldehyde with 90% product yield and 98% product selectivity was achieved under solvent-free conditions and in diphenyl solvents by using phase transfer catalyst. The system is scalable, the catalyst and solvent are recyclable.