



Catalytic fluorination of 2-chloropyridine over metal oxide catalysts in gas phase in the presence of HF

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ARTICLE INFO

Article history:

Received 20 June 2011

Received in revised form

21 September 2011

Accepted 2 November 2011

Available online 11 November 2011

Keywords:

Basic metal oxides

Fluoride metal catalyst

Fluorination

2-Chloropyridine

2-Fluoropyridine

ABSTRACT

The fluorination of 2-chloropyridine to produce selectively 2-fluoropyridine by Cl/F exchange at 300 or 380 °C with HF as the fluorinating agent and a metal oxide as precursor of catalyst was investigated. The influence of the activation step under HF gas on the structural, microstructural and physico-chemical properties of various oxides such as MgO, CeO₂, Ce_{0.5}Zr_{0.5}O₂, LaFeO₃, Cr₂O₃, were studied. This activation step by HF led to the formation of the corresponding fluorides and/or oxyfluorides materials which were the active catalysts for the Cl/F exchanges. Moreover, this activation step modified strongly the initial properties of the starting materials. This corresponded to a strong decrease of the initial specific surface area and of the basic properties. In the same time, an increase of Lewis acid properties measured by FTIR with pyridine as probe molecule was noticed. MgO, which was initially the most basic oxide studied was also the most active for the fluorination of the 2-chloropyridine after its transformation into fluoride solid which was the active catalyst. This could be due to a lower strength Lewis acidity of the active sites formed by the activation step by HF directly correlated to the basic properties of the initial oxides. A mechanism of the 2-chloropyridine fluorination involving Lewis acid unsaturated metal site was proposed.

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1. Introduction

Fluorinated aromatic compounds are used as building blocks in synthesis of pharmaceutical and agrochemical applications. The presence of fluorine atoms increases the lipophilicity of the compounds and the biological activity [1]. Specifically, fluoropyridine compounds are intermediates in the preparation of biologically active compounds such as herbicides, plant growth regulators, insecticides and fungicides [2].

Fluorinated aromatic compounds are mainly synthesized by HALEX reaction in liquid phase with KF [3–5] as the main fluoride source or by Balz–Schiemann reaction [6,7] in the presence of HF. Different substituted fluoropyridines, such as 2-fluoropyridine, 3-fluoropyridine, 4-fluoropyridine, 2,6-difluoropyridine, 2-fluoro-3-chloropyridine, 2-fluoro-5-trifluoromethylpyridine, 2-fluoro-6-methylpyridine, 4-ethyl-6-fluoropyridine, 2-chloro-6-fluoropyridine, 2-bromo-6-fluoropyridine and 3,5-dichloro-2,4,6-trifluoropyridine can be specifically synthesized by HALEX [8–21] or by Balz–Schiemann reactions [7,22–27]. However, these two reactions present limitations. The HALEX reaction is limited to substrates with an electroattractor group in ortho or para position with chlorine substitution, which severely limits its scope. Moreover, HALEX reaction leads to the formation of large amounts

of saline effluents (KCl). Anilines used as starting materials in Balz–Schiemann reaction, are generally very toxic and their transformations to produce the corresponding fluorinating compounds, involve more than one step. Finally, the yields are often low for both reactions.

Taking into account the limitations mentioned above, new access roads to industrial fluorinated aromatic compounds are an important issue. The aromatic nucleophilic substitution reactions in heterogeneous catalytic gas phase process from the corresponding chlorinated aromatics using HF as a source of fluoride have many advantages. The chloroaromatics are commercially available, generally less toxic than the corresponding anilines. The Cl/F exchange requires only one step and the only by-product is HCl (potentially recyclable).

Only few studies mainly in patent literature describe the fluorination of aromatics involving gas phase processes although promising [28–38]. Rader and Robota [28] disclosed a gas-phase process with HF gas at 350 °C to produce p-chlorobenzotrifluoride from p-chlorobenzotrifluoride over alumina fluoride catalyst. Scott and Ramsbottom [29] claimed a gas-phase process to produce fluorobenzene from chlorobenzene and 1-chloro-3-fluorobenzene from dichlorobenzene at 300 °C in presence of HF gas over a perfluorinated zinc chromite catalyst. However, the yields were low (5% of fluorobenzene and 10% of 1-chloro-3-fluorobenzene). Fujioka et al. [30,31] proposed a process to produce different fluoroaromatics such as o-chlorofluorobenzene, 2,6-difluorobenzonitrile or several perfluoropyridine from the corresponding chloroaromatics

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