Synthesize of AlF_3 as a catalyst of Heck reaction

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Abstract

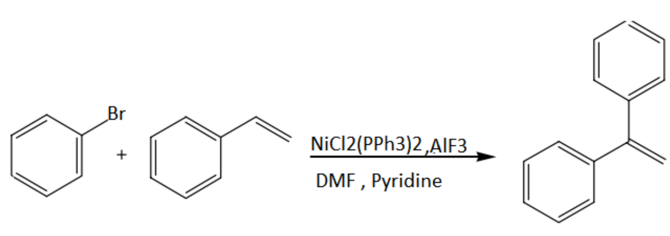
Aluminum fluoride has been widely used in industrial fields, for example it can be used as a catalyst for the synthesis of fluorocarbons and is used as a catalyst or co-catalyst in fluorination. In recent years, the use of this material in the technology of rechargeable lithium-ion batteries is of great importance. It is produced in white crystalline powder. Aluminum fluoride contains various phases such as α, β, η, κ, θ. All of these crystalline phases contain octahedral [AlF_6] units that form three-dimensional networks, but with different links in composition. The thermodynamic phase is stable α-AlF_3 and the other phases are metastable. Our goal is to produce aluminum fluoride using a fast and HF-free method. In this paper, the synthesis of AlF_3 by the incineration method was investigated. Aluminum nanoparticles powder was obtained by the ball-mill method of aluminum scraps and by mixing with polytetrafluoroethylene and burning their composition, AlF_3 crystals were created in the carbon. The X-ray diffraction pattern as well as the IR spectrum analysis confirmed this claim. It is expected that we will be able to use this material as a catalyst in organic reactions such as the Heck reaction and improve its performance using cocatalysts.

Keywords: AlF_3, Aluminum fluoride, Heck reaction, Ball-mill method.

1. Introduction

Most chemical production processes are catalyzed and in most cases heterogeneous catalysis reactions occur. Typically, Lewis acid catalysts such as aluminum halides as organic catalysts increase alkylation reactions, acylation, isomerization, electrolytic reactions, and elimination reactions [1]. Aluminum fluoride is mainly used in industrial applications and is used as a catalyst or co-catalyst for fluorination [2]. Aluminum fluoride, like many other fluoride metals, is a material with a high band gap and low refractive index, due to these properties, aluminum fluoride thin foils have many potential applications in the UV range [3]. In recent years nano-sized AlF_3 has attracted a great deal of attention in rechargeable Li-ion battery technology and has been used as a useful additive to enhance the chemical performance of lithium batteries [4]. The structural phases of aluminum fluoride are very diverse. The α-AlF_3 phase is the thermodynamically stable phase and consists of octahedral [AlF_6] units. This form crystallizes with the rombohedral structure of the R_3c space group [5]. The easy, fast, and bulky manufacturing of composite materials consists of carbon nanotubes doped with metallic compounds. Synthesis of carbon-aluminum fluoride composite foam (C-AlF_3) can be accomplished by using a combustion synthesis procedure, moisture-free method [4].

In this paper, the structural phase identification of aluminum fluoride synthesized by combustion method was investigated by X-ray diffraction pattern and IR analysis. The Heck reaction between styrene and bromobenzene was catalyzed by palladium bound to porous aluminum fluoride [2]. CC coupling reactions like Heck reactions (Scheme 1) are of growing interest for organic synthesis and fine chemical industry. Advantages of this reaction are a broad availability of aryl bromides and chlorides and the tolerance of a wide variety of functional groups. The Heck reaction is typically catalyzed by Pd complexes in solution. The application of this substance in the hacking reaction along with the nickel complex was also investigated [6]. We found that nickel complexes catalyse the condensation of styrenes with aryl and alkyl bromides in the presence of pyridine in N,N dimethylformamid. The $(Ph_3P)_2NiC1_2$ complex, was prepared following a known procedure [7].



Scheme 1. Heck reaction.

2. Materials and methods

In this project, aluminum fluoride was synthesized by combustion method. Initially, aluminum nanoparticles were obtained by ball mill method from aluminum scraps. 0.9 g of polytetrafluoroetylene (PTFE) and 0.45 g of aluminum nanoparticles (nAl) were measured and transferred to the affinity ball mill. The precursors were incubated for 3 minutes and transferred to a stainless steel container, heated to 160 °C, to allow the nanoparticles to disperse well into the polymer. Thereafter, using a butane heat burner, each piece of solid mixture was exposed to the flame directly and the combustion reaction was carried out with intense spark and light. The resulting black powder indicates the formation of the combustion reaction and the formation of AlF_3 nanoparticles within the carbon matrix, which was confirmed by the XRD pattern. Other products are mainly CF_4 gas, CO and a small amount of HF gas.

Bromobenzene and styrene were selected as precursors in the hacking reaction. Pyridine was selected as base and DMF as reaction solvent. Nickel complex was used as catalyst. The reaction was carried out under nitrogen gas at 140 °C. The reaction was synthesized once in the presence of aluminum fluoride and again without it.

3. Results and discussion

3.1. Characterization

3.1.1. SEM images of C-AlF_3 composite

Fig. 1 shows SEM image of the structure of C-AlF_3 nanocomposite. The morphology shows the distribution of aluminum fluoride particles uniformly with sub-nano dimensions within the carbon network. So that there is an open network with a set of pores.

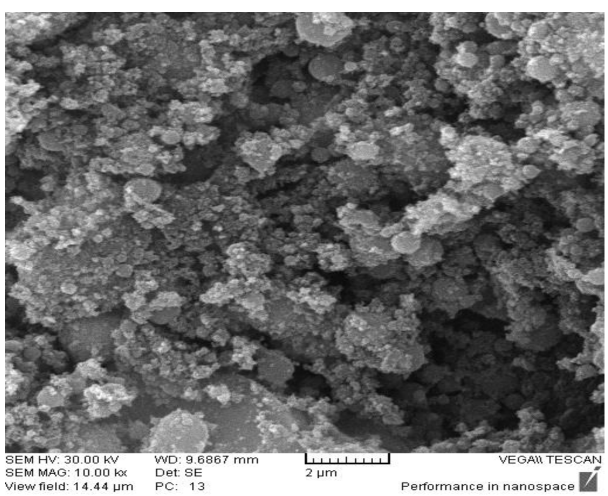


Fig. 1. SEM images of the structure of C-AlF_3 composite.

3.1.2. FT-IR spectra of C-AlF_3 composite

The FT-IR spectra of prepared nanocomposite aluminum fluoride in Fig. 2. The absorption band of α-AlF_3 is seen in around 650 cm^{-1}.

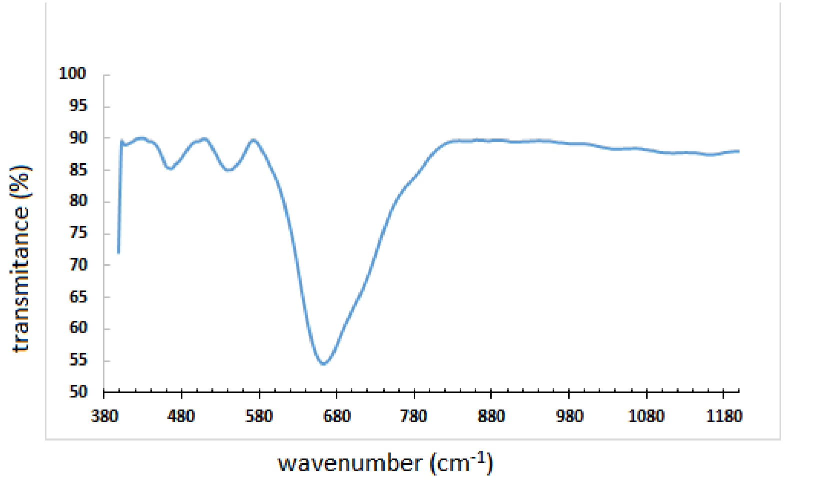


Fig 2. Transmission IR spectra of α-AlF_3.

3.1.3. XRD pattern of C-AlF_3 composite

Fig. 3 shows the X-ray powder diffractograms of crystalline α-AlF_3 phase. The powder pattern is in agreement with those published in the literature [4]. The dominant diffraction peak at 2θ~25.25° clearly corresponds to the α-AlF_3 rhombohedral crystal phase.

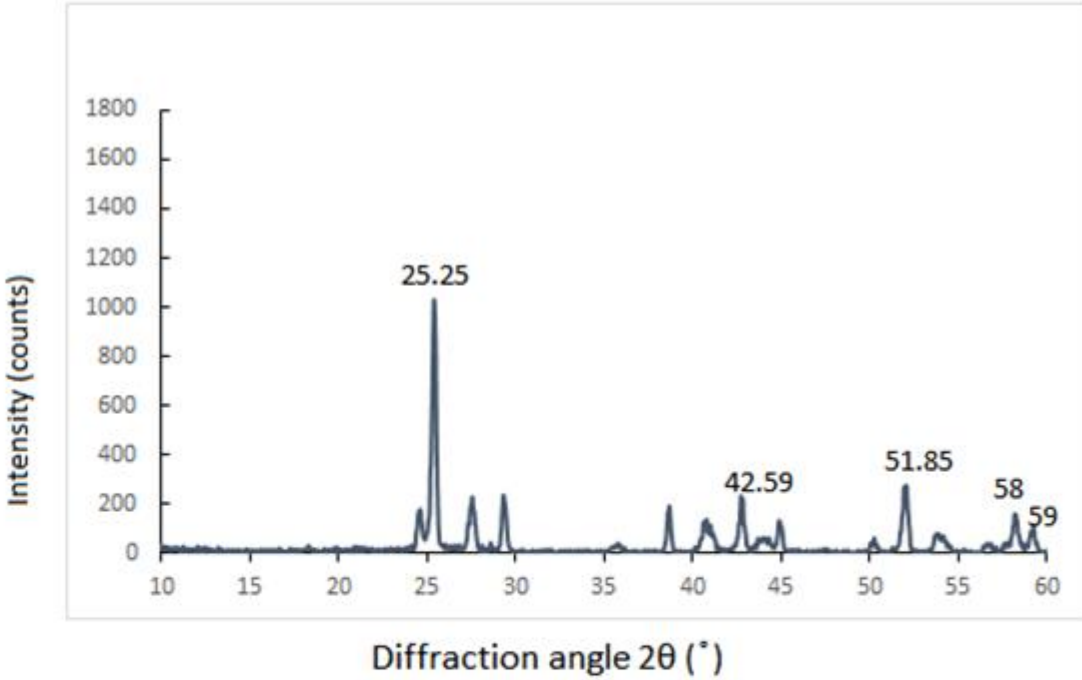


Fig. 3. X-ray powder diffraction pattern of aluminum fluoride composite (C-AlF_3).

3.2. The Heck reaction

The catalytic system $(Ph_3P)_2NiC1_2$/pyridine in acetonitrile is an effective catalyst for the Heck reaction (reactions of aryl and alkyl bromides with an alkene for example styrene to form a substituted alkene). With styrene, the reaction yields viny1 hydrogen replacement (condensation) products stilbenes and *p*-alkylstyrenes. Stilbene may refer to one of the two stereoisomers of 1,2-diphenylethene: (*E*)-tilbene (*trans* isomer) and (*Z*)-Stilbene (*cis* isomer).

In our work, in the presence of different catalysts different results were obtained. The results were listed in Table 1 show that the presence of C-AlF_3 composite has an important effect on reaction mechanism.

Table 1. The results of Heck reaction in the presence of different catalysts.

Catalyst	Products	Selectivity
C-AlF_3 composite	-	-
$(Ph_3P)_2NiC1_2$	Trans-Stilbene	100%
$(Ph_3P)_2NiC1_2$ + C-AlF_3 composite	Cis-Stilbene	100%

4. Conclusion

The purpose of this work was to produce aluminum fluoride by a fast and simple method. It was produced at high temperature under the butane flame in carbon dominance and was used in a hacking reaction with nickel catalyst to evaluate its performance.

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