



# Inorganic hydroxide fluorides as solid catalysts for acylation of 2-methylfuran by acetic anhydride

Fatima Frouri, Stéphane Célérier\*, Philippe Ayrault, Frédéric Richard

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR CNRS 7285, Faculté des Sciences Fondamentales et Appliquées, Université de Poitiers, 4, rue Michel Brunet, Bat B27, TSA 51106, 86073 Poitiers Cedex 9, France

## ARTICLE INFO

### Article history:

Received 27 November 2014  
Received in revised form 13 January 2015  
Accepted 17 January 2015  
Available online 20 January 2015

### Keywords:

Aluminum hydroxide fluoride  
Bi-acidic solid catalyst  
Acylation  
2-Methylfuran  
2-Acetyl-5-methylfuran

## ABSTRACT

Several inorganic hydroxide fluorides  $MF_{n-x}(OH)_x$  with  $M$  being either aluminum, iron, or magnesium were synthesized using a sol–gel method. These mesoporous fluoride materials exhibited very high specific surface areas (between 60 and 370  $m^2 g^{-1}$ ) depending on the synthesis parameters used (nature of the metal, HF/Al ratio, and thermal treatment). It is shown that their acidic properties can also be adjusted by tuning these parameters. Indeed, in the case of aluminum hydroxide fluorides, bi-acidic catalysts containing both Brønsted and Lewis acid sites were obtained, the amount of acid sites and the Lewis/Brønsted ratio (in the range of 1.9–7.6) being very dependent on the synthesis parameters. For example, the increase of the calcination temperature of aluminum hydroxide fluorides led to a decrease of both Lewis and Brønsted acid site, but also an increase of the Lewis/Brønsted ratio. The most acid fluoride exhibited 542  $\mu mol g^{-1}$  of Lewis acid sites and 291  $\mu mol g^{-1}$  of Brønsted acid sites.

These inorganic hydroxide fluorides were successively used as catalysts for the solvent-free acylation of 2-methylfuran by acetic anhydride under mild conditions (50 °C, atmospheric pressure) yielding selectively 2-acetyl-5-methylfuran. The activity of fluoride can be related to the amount of both Lewis and Brønsted acid sites. In general the higher these values, the greater the activity in acylation. A reaction mechanism was proposed involving a bi-acidic site which could be a Lewis acid site (unsaturated aluminum) in the vicinity of a Brønsted acid site.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Today, the investigation of new and alternative methodologies for the production of chemicals using low environmental impact technologies than those currently available is a major challenge for the scientific community. In this way, lignocellulosic residues can constitute a highly promising raw materials for the production of chemicals. For example, furfural can be produced by hydrolysis and dehydration of xylan which is a polysaccharide contained in hemicellulose [1]. This compound is considered as a promising platform molecule, since it can be used for the synthesis of several non-petroleum derived chemicals and fuels [2–5]. For example, furfural can be selectively hydrogenated into 2-methylfuran over metallic catalysts [6]. Its valorization into higher-value added products could be performed through Friedel–Crafts acylation reaction, since ketone functional group containing heterocyclic aromatic com-

pounds are known to be valuable intermediates of pharmaceutical chemistry [7].

Traditionally, the Friedel–Crafts synthesis is carried out in liquid-phase by using either protonic (HF,  $H_2SO_4$ ) or Lewis acids ( $AlCl_3$ ,  $FeCl_3$ , and  $TiCl_4$ ) as catalysts [8]. Nevertheless, the commonly encountered drawbacks of such a synthesis include the difficulty of catalysts separation and problems of waste disposal.

In the line with more stringent environmental legislation from the last years, the search for highly efficient and cleaner processes often leads to the replacement of homogeneous catalysts by heterogeneous catalysts [9]. Indeed, the use of solid catalysts offers definite advantages compared to homogeneous catalysts, since the former are easy to recover by simple filtration and produce no salts. In this way, the development of new and increasingly efficient solid catalysts for Friedel–Crafts acylation can be considered as a challenging task, particularly to address problems mentioned above.

Several acidic zeolites, like HZSM-5, HY, and H $\beta$  were often used as catalysts for the acylation of oxygenated heterocyclic compounds, such as furan [10,11] and benzofuran [12–14]. For example, the acylation of furan by acetic anhydride in vapour phase (150 °C,

\* Corresponding author. Tel.: +33 549 453 674; fax: +33 549 453 899.  
E-mail address: [stephane.celerier@univ-poitiers.fr](mailto:stephane.celerier@univ-poitiers.fr) (S. Célérier).

atmospheric pressure) over both HZSM-5 and HY zeolites led selectively to 2-acetylfuran with yields of 37 mol% and 21.6 mol%, respectively [11]. Over H $\beta$  zeolite, under milder experimental conditions (liquid phase, 60 °C, atmospheric pressure), in presence of a large excess of acetic anhydride (ratio furan to acylating agent of 5), 2-acetylfuran was also selectively synthesized with a yield of 91 mol% after 120 min [10]. Nevertheless, zeolites are known to be very sensitive to deactivation, especially when they were used as catalysts for acylation [14–17]. For example, the strong deactivation of the H $\beta$  zeolite observed during the acylation of anisole with acetic anhydride was mainly attributed to a strong adsorption of the mono-acylated product (*p*-methoxyacetophenone) on the acid sites [15]. A pore blocking by polyacylated products would also explain a part of the zeolite deactivation [15,16].

In the past decade, metal fluorides, such as MgF<sub>2</sub> and AlF<sub>3</sub>, with significant surface areas were successfully used in different heterogeneous catalytic processes with promising results as catalysts [18–23] and supports [24–27]. Specifically, in 2003, Kemnitz et al. have developed a sol–gel synthesis leading to the formation of amorphous aluminum fluoride with very high specific surface area and very high Lewis acidity [28]. From this first work, this group declined this synthesis method to the development of several nanoscopic metal fluorides or hydroxide fluorides MF<sub>*n-x*</sub>(OH)<sub>*x*</sub> with different acid–base properties [29–33]. Thus, by altering the synthesis parameters (fluoride – metal ratio, nature of metal, and amount of water during the synthesis), the authors showed that the strength and the nature of acid and basic properties (Brønsted and Lewis) might be adjustable.

Bi-acidic fluorine containing solids prepared by sol–gel method have been used recently as catalysts for Friedel–Crafts alkylation allowing the synthesis of two vitamins (K<sub>1</sub> and K<sub>1</sub>–Chromanol) in high yields (between 58 and 71 mol%) [34]. The alkylation of various aromatic compounds (benzene, ethylbenzene, trimethylhydroquinone, and menadiol) with isophytol and benzyl alcohol under mild conditions (100–120 °C) was also investigated over MgF<sub>2</sub> and AlF<sub>3</sub> catalysts [35]. Both solids were found as efficient catalysts for the synthesis of diphenylmethane and *p*-ethylidiphenylmethane. In the same way, menadiol was selectively acylated by an excess of acetic anhydride into menadiol diacetate at 80 °C over AlF<sub>3</sub> and MgF<sub>2</sub> [36].

As the development of clean catalytic processes is an important topic of environmental protection, we propose to develop the use of metal hydroxide fluorides MF<sub>*n-x*</sub>(OH)<sub>*x*</sub> (*M* = Al, Mg, and Fe) as bi-acidic solid catalysts for the synthesis of 2-acetyl-5-methylfuran. For this purpose, the acylation of 2-methylfuran by acetic anhydride was carried out under mild experimental conditions (50 °C, atmospheric pressure) over these catalysts. Their acidic properties were adjusted by modifications of some parameters of the catalyst synthesis: nature of the metal, Fluorine/Metal ratio, and thermal treatment. Based on their extensive characterization (obtained by nitrogen adsorption, XRD, TEM, and adsorption of pyridine followed by FTIR) and their catalytic properties measured in Friedel–Crafts acylation, some proposals concerning active sites involved and reaction mechanism were discussed.

## 2. Experimental

### 2.1. MF<sub>*n-x*</sub>(OH)<sub>*x*</sub> hydroxide fluorides synthesis (*M* = Al, Mg, Fe)

Caution: HF is hazardous; protection required.

AlF<sub>3-x</sub>(OH)<sub>*x*</sub> powders were prepared by sol–gel method, partly based on the work of Coman et al. [37]. In a first step, 4.9 g of aluminum isopropoxide (Aldrich, ≥98%) were introduced in 150 mL of methanol (Sigma–Aldrich, ≥99.9%) and after stirring during 20 min, stoichiometric amount of aqueous HF (3.02 g, 48–wt% HF in water,

Sigma–Aldrich, 99.99%) was added to this suspension under stirring conditions. After addition of HF, this solution was stirred during 8 h and aged at ambient temperature for one night. Then, the obtained sol was dried in an oven at 100 °C for 24 h to obtain a white powder, named AlF<sub>3</sub>-100 (where the number corresponds to the drying temperature). The AlF<sub>3</sub>-100 sample was then calcined under dry air at different temperatures between 150 and 350 °C during 5 h and the obtained powders were called AlF<sub>3</sub>-xxx where xxx corresponds to the temperature of calcination.

In some specific experiments, sub-stoichiometric amount of aqueous HF was introduced to obtain two different HF/Al ratios: 2.9 and 2.5. These powders were then calcined under dry air at 150 °C during 5 h and named AlF<sub>2.9</sub>-150 (from the HF/Al ratio of 2.9) and AlF<sub>2.5</sub>-150 (from the HF/Al ratio of 2.5).

The synthesis of MgF<sub>2-x</sub>(OH)<sub>*x*</sub> powder by a sol–gel method was based on the work of Wuttke et al. [38]. In a first step, magnesium metal (1.56 g, Aldrich, 99.98%) was treated with an excess of anhydrous methanol (50 mL, Sigma–Aldrich, ≥99.8%) under reflux conditions for 6 h to form Mg(OCH<sub>3</sub>)<sub>2</sub> metal alkoxide solution. Then, stoichiometric amount of aqueous HF (5.3504 g, 48 wt% HF in water) was added to this solution under stirring conditions. A highly exothermic reaction was performed to obtain a sol (gel was not formed due to the stirring conditions). This sol was stirred for 24 h, aged at ambient temperature for 24 h and dried at 100 °C for 24 h to form the powder named MgF<sub>2</sub>-100.

The synthesis of FeF<sub>3-x</sub>(OH)<sub>*x*</sub> powder by sol–gel method is based on the work of Guo et al. [30]. In a first step, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (11.7 g, Sigma–Aldrich, ≥98%) was pre-treated under vacuum at 65 °C during 2 h to form Fe(OH)(NO<sub>3</sub>)<sub>3</sub>·2.2H<sub>2</sub>O. This powder was dissolved in 150 mL of anhydrous methanol (Sigma–Aldrich, ≥99.8%) and after stirring, 9.65 g of anhydrous methanolic HF solution (18 wt% HF in anhydrous methanol) were added to form a transparent sol. After stirring during 1 h, the sol was dried under vacuum at 70 °C to form a powder. This powder was calcined under dry air at 100 °C during 5 h and named FeF<sub>3</sub>-100.

### 2.2. Zeolite

The commercial HY zeolite (CBV740) was provided by Conteka. This solid was activated at 450 °C under dry air for 6 h before catalytic experiments.

### 2.3. Catalyst characterization

XRD analysis of material powders was carried out on a PANalytical EMPYREAN powder diffractometer using CuK $\alpha$  radiation source (K $\alpha$ <sub>1</sub> = 1.5406 Å and K $\alpha$ <sub>2</sub> = 1.5444 Å) in order to reveal the crystallographic structure of each sample. These patterns were collected with a 0.02° step and 120 s dwell time at each step between 15 and 70°. Phase identification was performed by comparison with the JCPDS database reference files.

Nitrogen adsorption–desorption was performed at –196 °C using a TRISTAR 3000 gas adsorption system. Prior N<sub>2</sub> adsorption, the powder samples were degassed under secondary vacuum for 12 h at 70 °C. The BET equation was used to calculate the surface area (*S*<sub>BET</sub> in m<sup>2</sup> g<sup>-1</sup>) of the samples at relative pressures between 0.05 and 0.30.

The average pore size (*d*<sub>p</sub> in nm) was obtained from the desorption branch of the N<sub>2</sub> adsorption–desorption isotherm using Barret–Joyner–Halenda (BJH) approach.

The morphology of AlF<sub>3-x</sub>(OH)<sub>*x*</sub> powders was evaluated by Transmission Electronic Microscopy (TEM), using a JEOL 2100 instrument (operated at 200 kV with a LaB<sub>6</sub> source and equipped with a Gatan Ultra scan camera).

The acidity of solid materials was measured by adsorption–desorption of pyridine followed by FTIR spectroscopy

Download English Version:

<https://daneshyari.com/en/article/6500483>

Download Persian Version:

<https://daneshyari.com/article/6500483>

[Daneshyari.com](https://daneshyari.com)