

## Reduced coke formation during the gas phase oxidative dehydration of glycerol over ferrierite zeolites synthesized in fluoride medium



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### ABSTRACT

Ferrierite zeolites were synthesized in fluoride medium with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios 18, 22 and 37, using n-butylamine and pyridine as structure directing agents. The use of fluoride medium as mineralizing agent resulted in the formation of large crystals with morphology quite different from those obtained in hydroxide medium. These materials were characterized and evaluated in the gas-phase catalytic oxidative dehydration of glycerol at 300 °C, using air as carrier gas. Despite a low density of acid sites, the catalysts synthesized in fluoride medium led to high glycerol conversions and acrolein selectivities. Furthermore, coke formation was lower than that observed over the ferrierite synthesized in hydroxide medium.

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### 1. Introduction

The use of zeolites as catalysts in the glycerol dehydration has been extensively studied in the last years as a promising sustainable way to produce acrolein and other valuable products from glycerol obtained as a co-product of biodiesel [1,2]. Their catalytic performance is mainly due to acidic and textural properties, but different zeolite topologies, showing specific channels and/or cavities sizes, promoted different selectivity to the desired product [3]. Some results in the literature indicate that decreasing the pore size leads to higher selectivity, while the increase of the pore diameter, as well as the acidity, leads to higher conversions, but also to rapid deactivation by formation of carbonaceous deposits on the surface, blocking the acid sites [4]. This limitation can be partially overcome through two strategies: i) by adjusting the catalyst composition and/or properties; or ii) by changing operational parameters of the process. Thus, alternative strategies are: cycles of coke burning in

the presence of an oxidizing atmosphere after each reaction run [5], co-feeding air during the reaction run [6] or using a moving-bed reactor [7].

Many other studies have been performed using different catalysts, such as heteropolycompounds [8], mixed metal oxides [9–11] and phosphates [12–15], but deactivation by coke formation is still a general and serious limitation. Accordingly, the oxidative dehydration of glycerol has been used as the main strategy to avoid coke formation by limiting adsorption of heavy carbon species [6,13].

Recently, Park et al. [16] developed a kinetic model for the catalyst deactivation by coke formation during the gas phase dehydration of glycerol. The results obtained with an H-ZSM-5 catalyst fitted well to the model, indicating that deactivation depends on the concentration of products. Thus, the carbonaceous compounds would be generated through consecutive reactions from primary products and coke formation is strongly dependent on catalytic properties, such as surface area, pore volume and acid site density, which decrease the internal diffusion of glycerol inside the zeolite micropores.

Among the zeolite catalysts investigated in the dehydration of glycerol to acrolein, H-ZSM-5 (MFI topology) has received greater attention, but other zeolite topologies also showed excellent performance, such as BEA (zeolite β), FER (ferrierite) or MWW (zeolite MCM-22) [3,5]. Comparing different zeolite topologies,

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Kim et al. [3] observed that H- $\beta$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ) catalyst presented higher conversions of glycerol than MOR, FER, MFI or FAU zeolites, but the best selectivity to acrolein was observed for H-ferrierite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 55$ ). Nevertheless, the micropores were completely blocked by carbonaceous deposits, causing a marked decrease of glycerol conversion and of acrolein selectivity after 2 h of reaction.

Carriço et al. [5] have demonstrated that MCM-22 zeolite can be as active and selective as ZSM-5 operating at similar conditions, but much more coke (ca. 25%) was deposited during 12 h of catalytic run, indicating that the catalyst pore volume influences the coke content. They have also shown that the catalytic performance can be regenerated by alternating cycles of reaction and coke burning under air feed.

However, among these alternative zeolite topologies, ferrierite favoured the highest selectivity to acrolein as well as lower coke formation, operating under nitrogen flow. The ferrierite structure consists of channels of 10-membered rings (MR), whose inner diameter is  $0.42 \times 0.54$  nm, intersected by perpendicular channels of 8 MR, which possess  $0.35 \times 0.48$  nm of free diameter. The intersection between the channels accessed by 8-rings and 6-rings creates a  $[5^8 6^6 8^2]$  cavity [17]. Ferrierite may be synthesized by using either hydroxide or fluoride medium, but the use of these mineralizing agents results in formation of materials with different acidic, morphological and textural properties [18]. Many applications of ferrierite synthesized in hydroxide medium have been reported in the literature. However, excepting for gas separation, there are not many studies on the application of this zeolite synthesized in fluoride medium [19]. Moreover, no report could be found in the current literature of its use in the glycerol dehydration or oxidative dehydration.

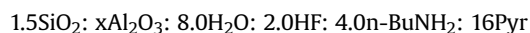
It is important to mention that fluoride media has been used to synthesize other zeolites, for example ZSM-5, using the variation of  $\text{F}^-/\text{Si}$  ratio as a strategy to tailor both crystal size and Brønsted acid sites [20]. Fluoride media synthesized ZSM-5 has also been investigated as catalysts for the conversion of methanol into light olefins [21], presenting better results than a sample prepared via the classical alkaline route ( $\text{OH}^-$  media).

In this work, ferrierite zeolites were synthesized in fluoride medium, evaluated in the gas phase oxidative dehydration of glycerol and compared to a ferrierite synthesized in hydroxide medium. The use of air as carrier gas was used as a strategy of obtaining long time stability of these catalysts.

## 2. Experimental

### 2.1. Preparation of the catalysts

The samples were prepared using pyridine (Pyr) and n-butylamine (n-BuNH<sub>2</sub>) as structure directing agents, by adapting the method proposed by Rakoczy et al. [22]. The following gel composition was used:



where  $x = 0.5$  to  $0.15$  depending on the desired values of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10, 15, 30$ ). The synthesis gels were prepared by adding 89.9 mL of pyridine (Sigma–Aldrich) and 27.5 mL of n-butylamine (Carlo Erba) in a polypropylene flask. The mixture was kept under stirring for 10 min and then 6.0 mL of 40% hydrofluoric acid (HF, F. Maya) was added dropwise. After that, 6.26 g of silica Aerosil 200 (Degussa) was added slowly under magnetic stirring, until obtaining a homogeneous, low viscosity and opaque gel. Then an appropriate mass of aluminium nitrate nonahydrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma–Aldrich), was added

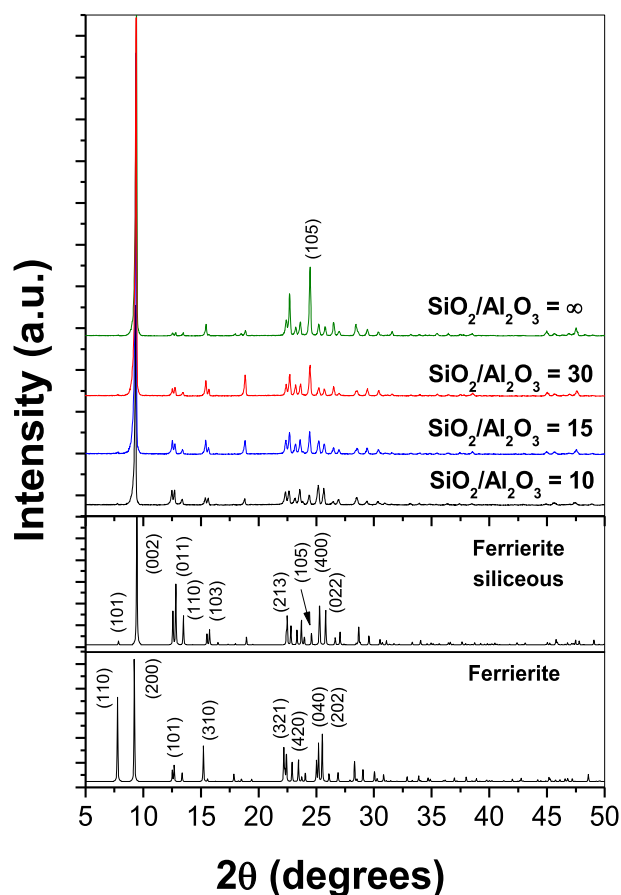


Fig. 1. XRD profiles of the ferrierite obtained in the fluoride medium, after calcination.

depending on the desired  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio. Finally, 6.4 mL of distilled water were added. The gels remained under stirring for 30 min, transferred to PTFE-lined stainless steel autoclaves and then hydrothermally treated at  $150^\circ\text{C}$  for 18 days. Afterwards, the powders were filtered, washed with deionized water until  $\text{pH} = 7$  and dried at  $80^\circ\text{C}$  overnight.

For comparison, a ferrierite sample with molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$  was synthesized using hydroxide medium, by adapting the method proposed by IZA Synthesis Commission [23], replacing silica sol by  $\text{SiO}_2$  Aerosil 200 (Degussa) and agitated synthesis at  $177^\circ\text{C}$  for 10 days by non-agitated crystallization at  $150^\circ\text{C}$  for 18 days.

Prior to calcination, the samples were analysed by thermogravimetry (TG) in order to determine the appropriate calcination temperature to allow the complete removal of the structure directing agents. The samples were then heated up to  $900^\circ\text{C}$  using a heating rate of  $1^\circ\text{C min}^{-1}$  and kept at this temperature for 6 h, under air flow of  $50\text{ mL min}^{-1}$ .

Aiming to assure that the samples were in the protonic form, the samples were ion exchanged with a solution  $0.1\text{ mol L}^{-1}\text{ NH}_4\text{NO}_3$

Table 1  
Elemental analysis by EDX and relative crystallinity by XRD.

$\text{SiO}_2/\text{Al}_2\text{O}_3$		Relative crystallinity (%)	Sample label
Nominal	Experimental		
10	18	63	H-FER(18)/63
15	22	67	H-FER(22)/67
30	37	62	H-FER(37)/62
$\infty$	2436	100	H-FER( $\infty$ )/100

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