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Chemometric Study of Microwave-assisted Hydrothermal Synthesis of Metal Organic Framework

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Abstract – Chemometric studies were performed for the synthesis of europium fumarate coordination polymers via microwave-assisted hydrothermal method. A full factorial planning 2^3 was conceived, considering the factors: time reaction, microwave intensity and presence of base. Only with addition of the base it was observed the formation of product. Moreover, microwave intensity is a relevant factor and higher intensities favours crystalline phase formation.

Metal Organic Frameworks (MOF's) have attracted a lot of attention not only because of their variety of architectures and topologies, but also due to their potential applications in gas storage[1a] and catalysis[1b], for instance. These materials have been synthesized under hydro(solvo)thermal conditions and this process takes 1 to 7 days[2]. Regarding the MOF Europium Fumarate, the literature reports that different synthesis methods lead to the same structure[3], $[Eu_2(Fum)_3.(H_2O)_4]_n.3nH_2O$, suggesting that this structure is the thermodynamically favoured one. In this context, this work proposes the microwave-assisted synthesis as a strategy to reduce time and cost. In order to optimize the process a chemometric approach was employed.

Eight experiments were performed in domestic microwave varying time, intensity and presence of base. The synthesis consists in the adding 0.3 mmol fumaric acid, 0.2 mmol $Eu(NO_3)_3{\cdot}3H_2O$ and in some cases (4 experiments) 0.6 mmol NaOH in 5 mL de-ionized water as shown in Table 1. A 12 mL Teflon® reactor was filled with the mixture and was placed in the microwave according to the conditions reported in Table 1. The samples obtained were characterized by Scanning Electron Microscopy (SEM), Powder XDR and Emission Spectroscopy. The results were compared with the MOF europium fumarate synthesized by hydrothermal method. Solid samples were obtained only in presence of NaOH (experiments 2, 4, 6 and 8), indicating that is a main factor in a synthesis of the europium fumarate. Samples produced in experiments 2, 4, 6 and 8 showed crystalline profiles, which is similar to the reference sample (obtained by hydrothermal method). However, some differences are observed in the XDR patterns (figure 1) as deviations in relative intensities and presence of extra peaks. Comparing the XDR patterns to reference sample it was observed that microwave intensity seams to play a relevant role and higher intensity favours crystalline phase formation. This material was, for the first time, observed by SEM and all samples presented lamellar rectangular shaped arrangements. However, higher intensity produces denser sample, where it was observed some pyramidal shaped particles. The emission spectrum (figure 2) reveals the formation of polymeric structures in the samples 4, 6 and 8 evidenced by large full width at half height of the $^5D_0 \rightarrow {}^7F_0$ transition (33, 41 and 32 cm^{-1}, respectively). In the compounds 6 and 8 (Figures 2C and 2D) it was observed the presence of more than one emitting species, since there are more than three and five lines for the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively, which could indicated the presence of isomers.

XDR patterns and emission spectra combined strongly suggest the existence of a crystalline europium fumarate framework, which was obtained under mild conditions.

Table 1: Experimental conditions

Experiment	Time	Intensity	Base
1	-	-	-
2	-	+	+
3	-	+	-
4	-	-	+
5	+	-	-
6	+	+	+
7	+	+	-
8	+	-	+

Time: 30 s (-), 60 s(+); intensity: 150 W (-), 300 W (+); base: absence (-); presence (+).

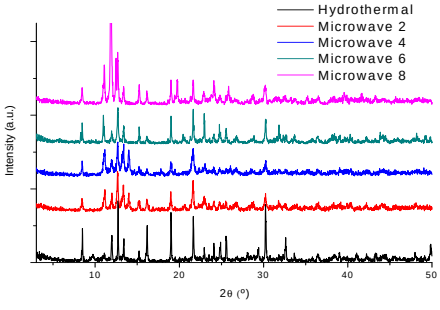

Figure 1: Powder XDR patterns of compounds hydrothermal, 2, 4, 6, and 8 (bottom to top, respectively).

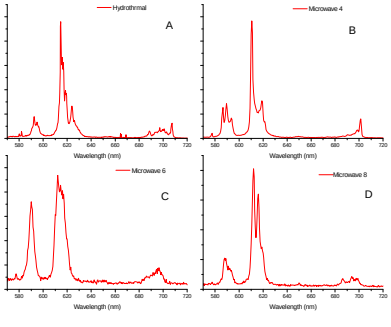

Figure 2: Emission spectra: Hydrothermal (A), microwave 4 (B), 6 (C) and 8 (D).

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