EFFECT OF THE SYNTHESIS METHOD ON THE PHOTOCATALYTIC ACTIVITY OF MULLITE-TYPE $Bi_2Al_4O_9$ TOWARDS THE VISIBLE-LIGHT INDUCED METHANOL OXIDATION

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In this work we employed and compared multiple synthetic methods for the preparation of the mullite type compound $Bi_2Al_4O_9$, aiming to explore its rather high photocatalytic activity, that has been recently reported. The resulting powders were characterized by means of a wide range of techniques including diffuse reflectance UV-Vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Finally, the photocatalytic activity of each sample was assessed by means of the oxidation reaction of aqueous methanol under irradiation with a monochromatic visible light source.

Materials that exhibit photocatalytic activity, i.e., that can use the energy of light to increase the rate of a chemical reaction, are a subject of abundant research nowadays due to their very useful applications. Among them we can cite mineralization of contaminants like polyaromatic hydrocarbons in environmental remediation[1], self-cleaning properties when they are applied as films, or synthetic uses as in the production of hydrogen gas by water splitting. In particular, mullite-type compounds of general formula $Bi_2M_4O_9$ (with M = Al, Fe, Ga) have achieved importance in this field, due to their optic and electronic properties[2,3], their low toxicity, low cost, and strong light absorption in the visible range of the spectrum[4], unlike some of the more commonly used photocatalyst, e.g., TiO_2, which absorb in the UV range (shorter wavelengths).

In this work, we focused our attention on the mullite-type compound $Bi_2Al_4O_9$, which has recently shown a relatively high photocatalytic activity. We employed and compared multiple synthetic methods for its preparation; all of them started from a common precursor solution containing the nitrates of bismuth and aluminum, which later goes through a thermal treatment including refluxing, calcining, etc. We studied (i) the effect of using additives such as polyvinyl alcohol (PVA, of varying chain length M_w) or glycerin, (ii) the effect of calcination temperature, and (iii) the use of a flame spray pyrolysis (FSP) procedure. Table 1 lists the information of each prepared sample.

Table 1: Synthetic specifications of each sample.

Sample	Additive	Heating conditions
PVA1	PVA (average M_w ~27000)	600ºC, during 30 min
PVA2	PVA (average M_w ~27000)	700ºC, during 2 hours
PVA3	PVA (average M_w ~ 61000)	600ºC, during 30 min
PVA4	PVA (average M_w ~ 61000)	700ºC, during 2 hours
GLY	Glycerin	750ºC
FSP	-	High but not constant temperature

Because the photocatalytic activity of a determined material is highly dependent of its physical properties[5], like specific surface area, degree of crystallinity and average crystallite size, a wide range of characterization techniques were used to assess these characteristic features on the resulting powders.

The phase composition, degree of crystallinity and crystallographic features (average crystallite sizes and lattice parameters) of the mullite-type $Bi_2Al_4O_9$ samples were determined by Rietveld refinements[7] of their X-ray diffraction patterns. The degree of crystallinity was found to be 35 to 85 % and the particle size between 15 and 35 nm Even though the mullite-type phase is expected to be the main one, others such as β-Bi_2O_3 may be present as well.

As complementary methods to the XRD analysis, we performed scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) measurements. This allowed not only the comparison of observed crystal size with the average value obtained via XRD, but also the determination of the presence of aggregates, which could cause a decrease in specific surface area and porous polycrystals. Effectively, particle sizes measured by the two methods, XRD and HR-TEM, were in agreement, and aggregates of various morphologies and in the order of micrometers were observed. For the determination of elemental composition, X-ray photoelectron spectroscopy (XPS) analysis was performed. The samples showed the expected bands for their constituting elements, in agreement with their chemical formula.

The samples were investigated by means of diffuse reflectance UV-Vis spectroscopy. The obtained reflectance spectra were transformed according to the Kubelka – Munk model[6] with the objective of determining the fraction of light absorbed by the powders at different wavelengths.

The photocatalytic characterization of each sample (see Figure 1) was carried out by means of the oxidation reaction of aqueous methanol under irradiation with a monochromatic visible light source (λ = 450 nm).

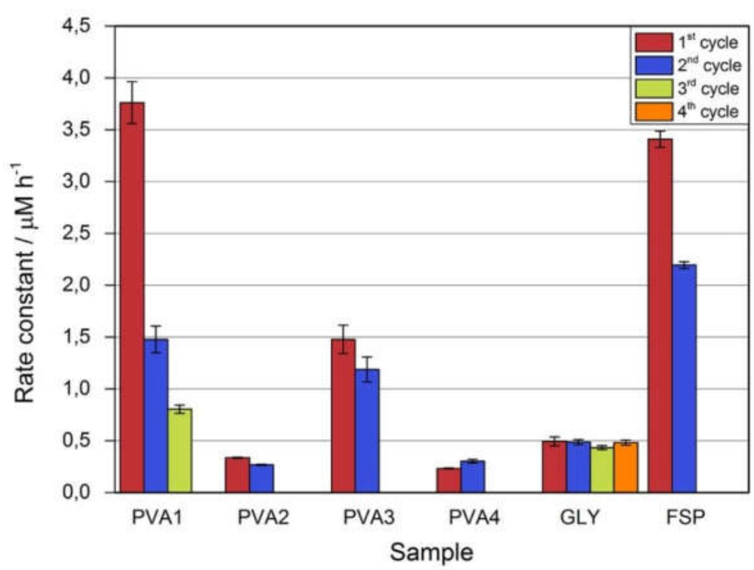

Figure 1: Rate constants for each sample in duplicate, triplicate and 4-times experiments.

The advantages of using methanol as a model compound to obtain information of a photocatalyst lie in two main aspects. On the one hand, the molecule in solution is colorless and, therefore, it does not absorb light in the visible range, so its reaction can be throws better results in comparison to dye decolorization, which is a widespread technique for the study of reaction kinetics. On the other hand, methanol is a simple and non-expensive compound, and its mechanism of degradation has been widely studied. The product of the oxidation, formaldehyde, was derivatized, and by means of a colorimetric method, the yellow product was quantified by UV-Vis spectroscopy. The rate constants obtained for each experiment using the different type of samples are shown in Figure 1. The synthetic procedure appears to be an important issue for the photocatalytic performance of the samples towards the methanol oxidation.

The use of a high calcination temperature and long heating times, as in samples PVA2 and PVA4, demonstrated to be detrimental, while the FSP procedure resulted in highly active materials. Samples containing large particles, those above or close to 35 nm, with lower exposed surface areas as compared to those with average particles size of 15 nm, show lower photocatalytic activities. Comparatively smaller particles, with higher exposed areas, are assumed to exhibit higher activities[1,8]. This is also attributed to the fact that the smaller the particles, the larger the number of surface and lattice defects, usually healed at high temperature treatments[8], and that may act as photocatalytic centers for the oxidation of the adsorbed methanol. It must be noted that samples PVA1 and FSP showed a systematic decrease in the photocatalytic activity, probably attributed to aging effects in these particular samples. In all other samples the photocatalytic activity could be reproduced (see GLY). The reasons for such a loss of activity are actually under investigation.

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