

A Flow–Through Membraneless Microfluidic

Zinc–air Cell

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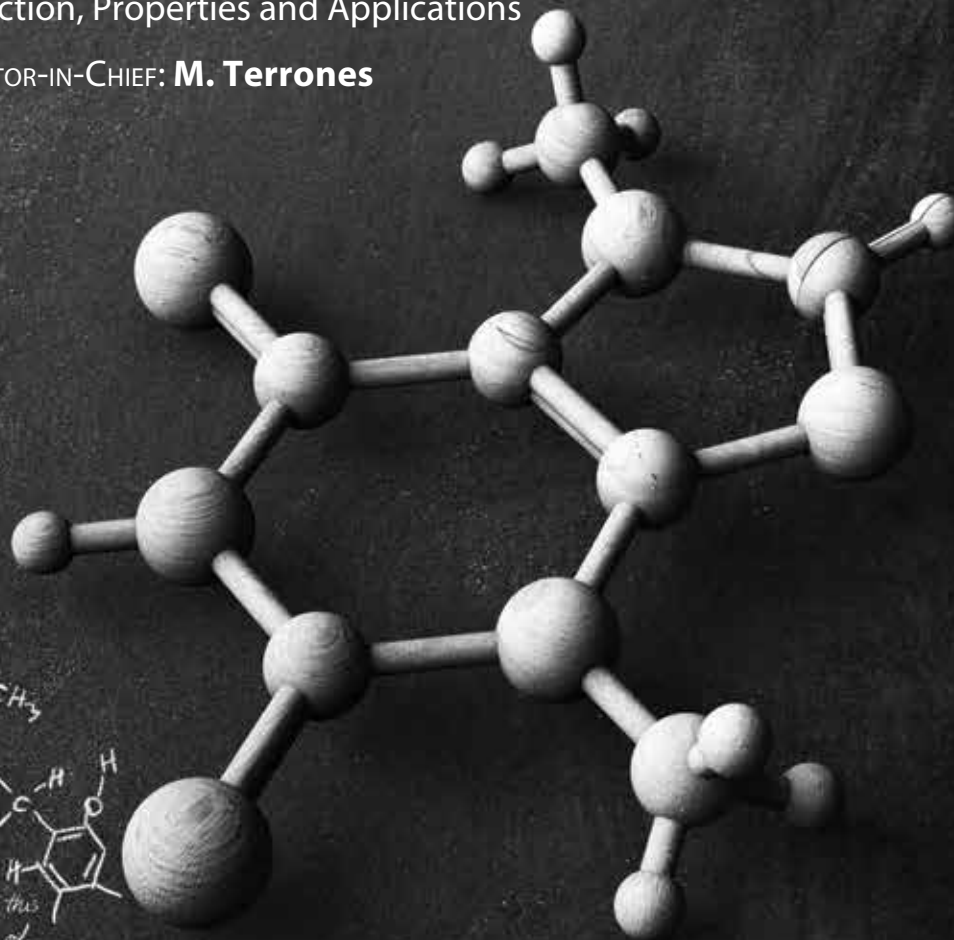
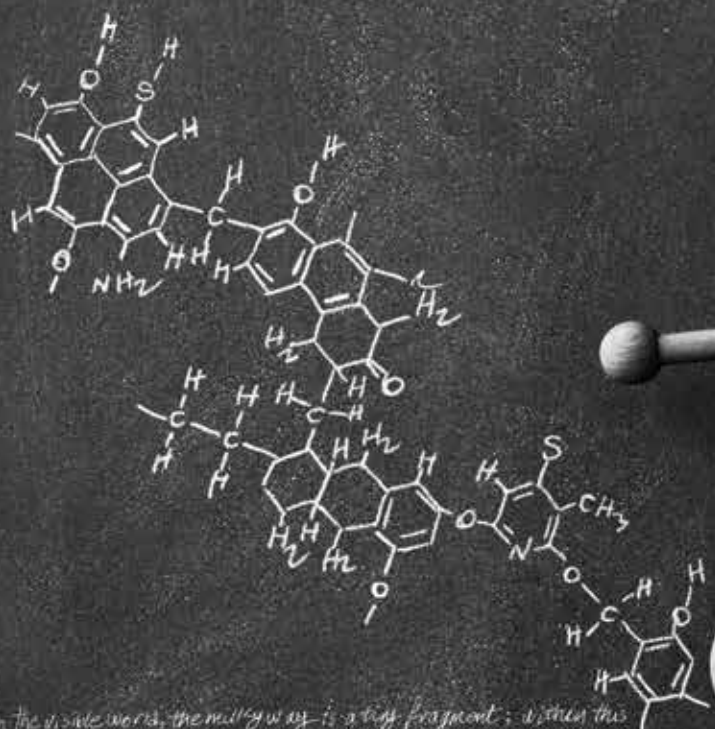
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“In the visible world, the milky way is a tiny fragment; within this fragment, the solar system is an infinitesimal speck; and of this speck our planet is a microscopic dot. On this dot, tiny lumps of impure carbon and water of complicated structure, with somewhat unusual physical and chemical properties, crawl about for a few years, until they are dissolved again into the elements of which they are compounded.”



Carl Sagan



Aging effect of plasma-treated carbon surfaces: An overlooked phenomenon

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Abstract

Carbon surfaces become significantly activated with plasma treatment enhancing the surface energy, wettability, and bio-conjugation. However, the activated surfaces are influenced by aging effect or reorientation phenomenon, a rarely reported occurrence, that refers to the loss of surface activity with time. Generated plasma-activated surface functional groups suffer from a brief shelf life as they reorient themselves to occupy lower states of energy. This study thoroughly assesses plasma-treated pyrolyzed carbon platforms with O₂, N₂, and Ar plasma radiations over 3 weeks. Pristine, immediately treated, and aged carbon samples were analyzed by SEM, AFM, WCA, and XPS to observe physical and chemical changes of the surfaces. Moreover, the electrochemical analyses demonstrated radical alterations of the surface characteristics immediately after the treatment; an activation which did not last long regardless of the plasma choice. With time, clear signs of surface inactivation were recorded manifesting in the form of decreased roughness, increased water contact angle, and major alterations of surface chemical composition, capacitance, and resistance. Our observations confirm that the plasma-treated carbon samples return to the pristine surface characteristics within a brief period of time thus demonstrating the loss of surface activity irrespective of the treatment choice.



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**Catalytic Engineered Materials
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Effect of the SiO₂ support morphology on the hydrodesulfurization performance of NiMo catalysts

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To study the effects of the support morphology on the hydrodesulfurization (HDS) activity of NiMoS catalysts, ordered mesoporous SiO₂ (KIT-6) and nonporous nanospheres of SiO₂ were used as supports. Metal species (Ni and Mo) were incorporated through a sequential impregnation technique. The aqueous solution of nickel nitrate was introduced first on the supports, followed by the solution of ammonium molybdate. Subsequently, a sulfidation treatment was carried out in gaseous H₂S/H₂ atmosphere. The NiMo/Al₂O₃ commercial catalyst was used as reference. The materials obtained were characterized by N₂ physisorption, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM) and evaluated in the HDS catalytic reaction of dibenzothiophene in a batch reactor. The results indicate that the textural properties of KIT-6 were the key factors to obtain disperse NiMoS stacks, and a better metal sulfidation, which lead to a higher catalytic activity of the NiMo/KIT-6 catalyst (twice as active) compared to the NiMo/Nanosilica catalyst. In addition, the activity of the NiMo/KIT-6 catalyst was also superior to that obtained for the commercial catalyst.

I. INTRODUCTION

The growing demand of high performance fuels, associated with environmental regulations and the continuous decrease in the quality of petroleum feedstock, demands the development of better catalysts for sulfur removal from diesel fuels, being this challenge one of the most significant for refining industry.

At present, catalysts based on transition metals that are used to treat crude oil fractions show low tolerance to sulfur atoms, leading to an accelerated deactivation and breakdown of the catalyst. Traditional hydrodesulfurization (HDS) catalysts are composed of active molybdenum or tungsten sulfides, promoted by cobalt or nickel and supported on alumina (–Al₂O₃).^{1,2} However, due to its limited activity, these catalysts present disadvantages when ultra-low sulfur diesel (ULSD) is required. Thus, to reach the low sulfur concentration established by the regulations, it is necessary to develop new HDS catalysts with improved activities.

In recent times, many efforts are aimed to improve the performance of hydrotreating catalysts, by using mixed oxides,^{3–7} zeolites,^{8–10} mesoporous molecular sieves,^{11–15} and clays,¹⁶ since the properties of the sulfide phase have been observed to be strongly affected by the nature of catalyst supports.^{3,11} The selection of the support has an important influence for catalyst final properties, such as

aging and deactivation resistance, regeneration, and ease of sulfidation, as well as the recovery of the spent catalysts.¹⁷

The variation of catalytic activity due to the support is the result of factors such as variation in dispersion and morphology of the active component as well as the metal–support interactions. The support can also affect the level of metal sulfidation and reactivity by fostering the exposure of some preferably crystallographic planes by edge bonding or basal plane bonding of the sulfide phase. The results in the activity and/or selectivity of the catalyst, due to metal support interactions and morphological characteristics, show that the support is an important component in the catalysts¹ and contributes to define the role of catalyst during the chemical reaction. The support has an indirect participation in determining the effect of promoters by altering the number of atoms that can be accommodated at the edges of the MoS₂ structure, and the energetic characteristics of the site where promoter is associated.^{1,18} Moreover, not only the chemical nature of the support is important but also the morphology of support since distribution of active sites on the surface and the way molecules reach those sites determines the activity and selectivity of catalysts.

There are many studies carried out on catalysts supported in alumina for HDS, and it has been found that strong metal support interaction that this system presents restrains its use as the HDS catalyst for the production of ULSD. This work aims to evaluate the effect of the support morphology on the catalytic performance of NiMoS catalysts; for this purpose, SiO₂ with two different morphologies were used: one is the ordered

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Microstructure Patterns by Switching Spectroscopy Piezo-response Force Microscopy of Lead Free Perovskite-type Polycrystalline Thin Films

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The purpose of this work is to perform DC-based manipulations as a nanolithography tool to fabricate nanostructured patterns on lead free ferroelectric thin films (TF) with stoichiometry $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (denoted in this work as BCZT), where $x = 0.1, 0.15$ and 0.2 . To establish the evidence of ferroelectricity in BCZT, one has to probe the local domain configurations and demonstrate the switching of the polarization [1]. For this material, the switching corresponds positively and negatively to the polarized regions [2], and as an example, we use the CIMAV logo as template, Fig 1a.

Polarization switching in polycrystalline BCZT bulk and thin films on Pt-coated substrates was studied by switching spectroscopy piezo-response force microscopy (SS-PFM) in dual AC resonance tracking (DART) mode. Fig. 1b and 1c show the switching domains before and after of the hysteresis loop measurement in the region marked with a blue circle on the PFM amplitude micrographs for the BCZT-TF with $x=1$. In these micrographs, the white region was polarized downward, whereas, the orange dotted region was polarized upward, confirming the 180° phase difference between the two domain configurations. The out-of-plane piezo-response was determined as a function of an applied voltage, and the PFM hysteresis loops, both in amplitude and phase are shown in Fig. 2a and 2b, respectively. Figure 2a exhibits a butterfly shape, whereas Fig. 2b reveals a sharp 180° inversion at the coercive voltages with a clear hysteresis. These results confirm the ferroelectric nature of BCZT-TF. The piezoelectric response d_{33} was determined by analyzing the local amplitude measurements “off-state” through the following equation $(V - V_1) d_{33} = D - D_1$ [3]; shown in Fig. 2c. BCZT-TF shows a $d_{33} = 2.2 \text{ pmV}^{-1}$ at the maximum voltage of 50 V and the coercive voltage was around 12.2 V.

To complement the characterization of these electro-ceramics, Fig. 3a and 3b show a comparison between the X-ray diffraction (XRD) for the target prepared modified Pechini method [4] and sintered at 1200°C for 5 h; and the grazing incidence XRD for BCZT-TF (obtained by radio frequency magnetron sputtering system), respectively. The Rietveld refinement for the XRD results suggest a perovskite-type structure with tetragonal phase ($P4mm$ space group), that is compatible with the ferro (Fig. 3c) - piezo electrical response. In summary, the polarization switching behavior in the ferroelectric BCZT-TF as a relevant tool to optimize the image of polarization reversal as a lithography technique to store nanostructured patterns was shown [5].

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POLYMER COATINGS

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Supporting Information

Super-Anticorrosive Materials Based on Bifunctionalized Reduced Graphene Oxide

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