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Solid state ^{27}Al NMR and X-ray diffraction study of alumina–carbon composites

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ABSTRACT

The structural and chemical transformations occurring in alumina–carbon composites upon heat treatment were investigated by using a combination of X-ray diffraction (XRD) and solid-state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy. Two different carbon precursors were employed: a commercial activated carbon and a char obtained by carbonization of the endocarp of babassu coconut at 700 °C. The alumina–carbon composites were prepared by aqueous impregnation of the carbon supports with aluminum nitrate and, after filtering and drying, the as-synthesized powders were heat-treated under argon flow at temperatures up to 1000 °C. The Al compounds present in the as-synthesized samples were identified by XRD and solid-state ^{27}Al NMR as nanocrystalline aluminum oxyhydroxides or hydroxides, depending on the synthesis conditions. All Al-containing phases were XRD-amorphous in the char-derived nanocomposites, with the presence of a distribution of AlO_6 (octahedral Al site), AlO_5 (pentacoordinated Al) and AlO_4 (tetrahedral Al site) units revealed by solid-state ^{27}Al NMR spectroscopy. The heat treatments caused the formation of transition aluminas dispersed over the carbon supports, with the occurrence of different amounts of AlO_6, AlO_5 and AlO_4 units depending on the heat treatment temperature and on the type of carbon precursor used for the preparation of the composites.

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1. Introduction

Composite materials containing metallic or oxidic nanoparticles supported on porous carbon materials have many technological applications in fields such as catalysis [1,2], magnetic separation [3], water cleaning [4] and others [1–4]. Depending on the characteristics of the carbon materials used as supports, carbon-supported nanocomposites may exhibit high surface area and good structural and thermal stability, precluding the agglomeration of the supported nanoparticles. These nanocomposites can be prepared by many different routes. Wet chemical methods are among the most used ones, allowing the synthesis of products with varied chemical and physical properties [5,6].

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Abbreviations: AC, commercial charcoal activated carbon; BC, char obtained by carbonization of the endocarp of babassu coconut; CT, central transition; DSC, differential scanning calorimetry; EDX, energy dispersive X-ray spectroscopy; EFG, electric field gradient; FID, free induction decay; MAS, magic-angle spinning; MQ-MAS, multiple-quantum magic-angle spinning; NMR, nuclear magnetic resonance; SEM, scanning electron microscopy; SPE, single pulse excitation; TG, thermogravimetry; XRD, X-ray diffraction.

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Porous carbon materials containing dispersed aluminum oxides are of interest for several applications, including the removal of fluoride from water [7,8] and the adsorption of ammonia from gaseous mixtures [9]. Moreover, alumina–carbon composites can also be used to support metallic catalysts, combining the positive aspects of both alumina and carbon as porous supports. For instance, an alumina-activated carbon composite was used to prepare supported NiMo catalysts, which showed better stability and enhanced activity for the reaction of hydrodesulfurization of dibenzothiophene, when compared to similar catalysts prepared on either activated carbon or alumina supports [10]. This effect was attributed to the mesoporous nature of the composite support and to the high dispersion achieved for the Ni and Mo species. A similar result of higher activity of NiMo/alumina–carbon black composite in the hydroconversion of a vacuum residue (hydrodesulfurization and hydrodenitrogenation reactions) when compared to an alumina-based commercial catalyst was attributed to the occurrence of macropores in the composite material (with 11–20% of pore volume) [11].

The properties of alumina–carbon composites depend on the physical, chemical and structural characteristics of the Al-containing phases and of the carbon support, as well on the possible interactions between them. To elucidate these features, a number of characterization methods are routinely applied, including X-ray diffraction (XRD), scanning electron microscopy (SEM), textural and thermal analyses [8,10]. Solid-state nuclear magnetic resonance (NMR) spectroscopy is a very useful tool for this kind of characterization, since it allows the assessment of information about the chemical environment of the chosen probe nuclei in a non-destructive way. Moreover, contrary to XRD and other diffraction-based techniques, solid-state NMR spectra can be successfully recorded for crystalline, nanocrystalline or amorphous phases, making possible the characterization of atomic environments even in structurally disordered and heterogeneous materials [12,13]. In this way, solid-state ^{27}Al NMR has been used for many years in studies of aluminas and related materials, including nanostructured templates, mesoporous supports, layered compounds, amorphous alumina nanoparticles, etc. [14–19]. One of the main findings derived from solid-state ^{27}Al NMR studies was the establishment of the thermal pathways leading from aluminum hydroxides or oxyhydroxides up to the most stable alumina phase (α-Al_2O_3, or corundum), passing through different transition aluminas (many of them presenting low degree of crystallinity) [20–25].

These investigations have been possible because ^{27}Al is a very favorable nucleus from the point of view of NMR spectroscopy, with a natural abundance of 100% and often quite fast spin–lattice relaxation processes that enable short delay times to be used and, thus, allow the achievement of spectra with good signal-to-noise ratio in relatively short measurement times [12]. However, with a nuclear spin of 5/2, ^{27}Al is a quadrupolar nucleus, with a sizeable electric quadrupole moment that interacts with any local electric field gradient (EFG) that exists at the nuclear site. This so-called quadrupole interaction contributes to large, anisotropic broadening of solid-state ^{27}Al NMR spectra in aluminum oxides and other compounds. On the other hand, it also expands the amount of information that can be gathered from the NMR spectra, since the quadrupole interaction is highly sensitive to the local structure around the nuclear sites [26].

In most typical cases, the ^{27}Al NMR spectra recorded with magic angle spinning (MAS) exhibit strong sets of spinning sidebands, associated with the satellite transitions, which span a very large frequency range. On the other hand, the resonance lines due to the central transition (CT) – i.e., between the energy levels with ±1/2 spin quantum numbers – are much narrower and thus these are the resonances most commonly observed and used for the analysis of Al compounds [12,26]. The shape and the frequency shift of these resonances are determined by the following spectral parameters: the isotropic chemical shift (δ_{iso}), the quadrupole coupling constant (C_q) and the asymmetry parameter of the EFG tensor (η_q). For crystalline materials, it is possible to determine these parameters for each Al site by spectral fitting of the observed CT lineshapes [12]. However, when there is some disorder in the Al environment (of either structural or chemical origin), the patterns are broadened and the features and singularities typical of the CT pattern are not directly observed. Particularly, the occurrence of variations in bond lengths and bond angles cause a distribution in the EFG parameters (C_q, η_q), which broadens the CT pattern in a quite typical fashion, leading to a pronounced asymmetry and a long tail developing towards the lower frequency side [12,15,17,22]. These broad patterns can also be fitted assuming a continuous distribution of the spectral parameters, thus revealing details about the type of disorder present in the material [15,18,22,27].

When the quadrupole interaction is present, the isotropic chemical shift of a peak in ^{27}Al MAS NMR spectra does not correspond to the peak position. Even so, it is possible in many cases to determine the δ_{iso} values associated with different sites, either by spectral fitting or by other methods such as the use of multiple magnetic fields [28] or multiple-quantum (MQ) MAS experiments [12]. In the case of materials containing Al–O linkages, the Al coordination number results in a number of characteristic chemical shift ranges [12,26]. In most alumina forms, Al sites are distributed among 4-coordinated (tetrahedral symmetry) and 6-coordinated (octahedral symmetry) sites. Typically, AlO_6 units are characterized by shifts in the range 10–15 ppm, whereas the shifts due to AlO_4 units fall in the range 50–80 ppm (with all shifts measured with respect to the ^{27}Al NMR peak of 6-coordinated Al^{3+} ions in aqueous solution) [12,20–24]. In transition aluminas presenting reduced crystallinity, AlO_5 units (corresponding to 5-coordinated Al in trigonal bipyramidal geometry) are frequently present, giving rise to broad resonances with chemical shifts falling somewhat between the above mentioned ranges, at about 30–40 ppm [12,19,20]. The relative contributions associated with these species can be computed from the integrated areas corresponding with each resonance, provided a reasonable fitting model is established and the correction factors associated with the distribution of intensity between the centerband and the spinning sidebands are taken into account [12,15,19,27,29,30].

In this work, the structural and chemical transformations occurring upon heat treatments in alumina–carbon

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