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Spent refinery catalyst as a synergistic agent in intumescent formulations: influence of the catalyst's particle size and constituents

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Abstract

Spent oil-cracking catalyst from the FCC process was incorporated into an ammonium polyphosphate and pentaerythritol intumescent mixture, both as received, and after milling and sifting. The influence of the catalyst's average particle size on flame retardancy performance was investigated by UL-94 rating standard, limiting oxygen index (LOI), thermogravimetric analysis (TGA) and cone calorimetry. The effect of each of the catalyst's components on the fire resistance of the final composite was also studied. The results show that the best flame-retarding properties are obtained with the finest catalyst fraction and that, of all its components, only the silica–aluminates, such as kaolin and zeolite, affect flame performance to a significant extent.

Keywords: Spent FCC catalyst; Flame retardancy; Intumescence; Ammonium polyphosphate; Pentaerythritol

1. Introduction

Intumescent additives are playing a significant role in the fire retardancy of polymers, especially when used in combination with other additives that lead to improved performance. The use of synergistic agents not only produces more efficient systems but also makes it possible to reduce the amount of flame-retardants employed while delivering efficient flame retardancy performance within the stringent regulations imposed [1]. Clays and zeolites [2–5] have been used with synergistic action in intumescent ammonium polyphosphate and pentaerythritol formulations.

The worldwide annual demand for fluid bed catalytic cracking (FCC) catalyst in oil refineries is around 300 thousand tons [6] and, while many forms of reutilization of the material have been suggested, only its use in the cement industry has gained any wide range industrial status [7]. Other forms proposed for the reutilization of the spent catalyst include its use in wastewater treatment [8,9], as an absorbent in dangerous liquid spillages [10], in the production of vitro-ceramics [11], in the recovery of heavy metal contaminants from the waste catalyst [12,13], as a catalyst in the pyrolysis of plastics [14,15] and in the production of 4A zeolites [16].

For many decades FCC has been one of the most important processes in oil refineries. The FCC unit aims

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at the conversion of heavy fractions from oil distillation (gas oils and resid fuels) into lighter fractions with greater economic value such as gasoline, diesel fuel and light gases [17,18]. Thus, the FCC process increases the proportion of specific fractions, in comparison with that obtained directly from the distillation process, for compliance with market demands. The process consists of the cleavage of heavy molecules into lighter compounds by the joint action of heat and a zeolite based catalyst. The inevitable coke formation on the surface of the catalyst and the adsorption of polar compounds on the reaction sites leads to catalyst deactivation. The catalyst is continuously regenerated by burning the coke off its surface with an air flow, and the nearly coke-free catalyst is recycled to join the fresh feed where the cycle recommences. However, the catalyst may also be irreversibly deactivated by particle sintering, collapsing of the crystalline structure, poisoning and fouling by vanadium, nickel and other metals from the feedstock [19–21]. To maintain the process, catalytic activity and selectivity, part of the catalyst inventory is periodically discharged and new catalyst is introduced into the process. The removed catalyst is known as spent catalyst, exhaust catalyst, discharged catalyst or equilibrium catalyst.

The FCC catalyst is typically composed of a zeolite embedded in a silica–alumina matrix. The zeolite crystals are responsible for the predominant activity and desired product selectivities, and because they represent the active phase of the material, a catalyst composed solely of zeolite would overcrack the feedstock. Thus, the matrix plays an important role in controlling the relative crackability and other properties of the catalyst. The matrix consists mainly of a binder, such as silica hydrosols or alumina gels, an active matrix component, usually alumina and a filler, typically kaolin clays. Specific components like vanadium and nickel traps may also be used but in a lower content than the other components. The catalytic action of the matrix enhances the cracking efficiency as a whole, since it can crack bulky organic molecules that cannot diffuse into the zeolitic pores. This pre-cracking of the large molecules generates smaller compounds, which are then able to undergo final cracking by the zeolite. The filler dilutes the activity of the active component as well as conferring desirable mechanical properties to the catalyst [18,22,23].

Zeolite Y was first introduced into the cracking catalyst in the early 1960s, revolutionizing the FCC process by increasing cracking activity and gasoline selectivity. Shortly after, ultrastable Y zeolites (USY) and rare earth exchanged zeolites (REY and REUSY) were introduced into the catalysts [24]. The USY zeolites are produced by removing framework aluminium from the zeolite Y structure [25]. This increases acid site strength of the zeolite and thermal/hydrothermal stability of the material. The properties of synthetic zeolites can also be improved by ion exchange with rare earth ions. These ions increase zeolite acidity by the protonic dissociation of water molecules, as well as improve the material's hydrothermal stability in the harsh conditions encountered in the regenerator [26].

Recently, the use of spent oil refinery cracking catalyst has also been proposed as a flame retardancy enhancer for intumescent formulations [27–29]. The use of this material as a synergistic agent has an added bonus of reducing environmental hazards due to waste discharge from refinery reactors while also reducing the cost of the final material.

In this study, we aim at a better understanding of some of the factors influencing the use of the waste catalyst as a synergistic agent in intumescent flame retardancy of polymers. The effect of the inorganic material's particle size is investigated by classical fire performance testing. In addition to this, the flame retardancy performance of each of the catalyst's components was studied individually in order to determine which of them exert modifications in the traditional ammonium polyphosphate and pentaerythritol intumescent systems. A comparison between different types of Y zeolite was made to try and observe how different counter ions and acidity influence flame retardancy performance of the intumescent systems.

2. Experimental

The polymer matrix used consisted of a copolymer of ethylene and butyl acrylate (PEBA), containing 30 wt% of butyl acrylate, supplied by Elf-Atochem. The choice of the matrix was based on previous studies, in which the synergistic action of the spent catalyst with intumescent additives was clearly demonstrated [28]. The intumescent additives used were ammonium polyphosphate (APP) supplied by Clariant under the tradename Exolit AP 422, and pentaerythritol (PER) from Acros.

The spent catalyst as received (E.Cat.) was submitted to ball milling for 7 h, followed by wet sifting in a mechanical shaker. The fractions collected using 150, 270, 400 and 635 Tyler mesh standard sieves were dried and used for further testing. The morphology of the various fractions was observed by scanning electron microscopy (SEM) using a Leica S440 microscope with a Si/Li Oxford detector. The samples were ion-sputtered with gold in an argon atmosphere.

The chemical compositions of the various fractions, and of the catalyst as received, were determined by X-ray fluorescence analysis using a Philips PW 1480 X-ray spectrometer, and the zeolite content of the samples was determined by X-ray diffraction in a Philips PW 1710 instrument with a copper anode, taking into account absorption variations due to the presence of