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The state of nickel in spent Fluid Catalytic Cracking catalysts

Guido Busca[a,*], Paola Riani[b], Gabriella Garbarino[a], Giovanni Ziemacki[c], Leonardo Gambino[d], Erica Montanari[e], Roberto Millini[e]

[a] Università degli Studi di Genova, Dipartimento di Ingegneria Civile, Chimica e Ambientale (DICCA), Laboratorio di chimica delle superfici e catalisi, P.le Kennedy 1, I-16129 Genova, Italy
[b] Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale (DCCI), Via Dodecaneso 31, I-16146 Genova, Italy
[c] Dipartimento Ambiente e Connessa Prevenzione Primaria, ISS, Italy
[d] ISAB S.r.l., Priolo Gargallo (SR), Italy
[e] Eni S.p.A., Development, Operations & Technology, Research & Technological Innovation Department, San Donato Milanese Research Center, Via F. Maritano 26, I-20097 San Donato Milanese (MI), Italy

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ABSTRACT

The speciation of Ni in spent Fluid Catalytic Cracking catalysts is studied. Carefully performed XRD analyses with NiO/SiO_2 samples used as calibration standards, demonstrate that the presence of NiO as a separate phase is reliably detected also for NiO concentration close to 0.1 wt% (1000 ppmw). Actually, both on real spent FCC catalysts (ECAT's) and on artificially contaminated industrial FCC catalysts, NiO is not detectable as a separate phase, even after contamination of the order of 15,000 ppmw of Ni. SEM–EDS experiments provide evidence of a largely preferential location of Ni on alumina particles present in the FCC catalyst mixture, thus acting as "nickel traps". XRD, UV–vis and TPR data confirm that Ni deposits on alumina particles forming a hardly reducible surface and subsurface layer, giving rise to a solid whose composition is $Ni_xAl_2O_{3+x}$ with $x \ll 0.25$. As a result of this, the formation of extended Ni metal particles in the raiser reactor is avoided, being their unwanted dehydrogenation activity essentially eliminated. The absence of bulk NiO in the spent FCC catalysts (at least when Ni content is in the range 2000–10,000 ppmw) allows the classification of this material as a non-hazardous waste.

1. Introduction

Catalysis is critical in the industry as demonstrated by the fact that ~90% of the chemical, petrochemical and oil refining processes involve at least a catalytic step [1]. The development of new transformation processes is linked to the availability of increasingly more efficient catalysts able of producing a given chemical with high productivity, selectivity (thereby limiting the formation of useless byproducts) and low energy consumption. The current trend is to prefer the heterogeneous solid catalysts with respect to the homogeneous ones, i.e. those operating in the same phase of the reagent mixture (for example, mineral or Lewis acids operating in the liquid phase for acid-catalyzed reactions). The advantages deriving from the use of solid catalysts are multiple: they typically have a high selectivity, do not present problems of corrosion, can be easily separated from the products, have a long life and can be regenerated several times without significantly losing their catalytic properties. The overall life of a solid catalyst depends on its characteristics and the process that is being used. During its life cycle, a solid catalyst deactivates gradually for several causes. A typical phenomenon concerns the deposition of heavy organic products, which make progressively inaccessible the active sites; in these cases the functionality is restored by calcining the deactivated catalyst under appropriate conditions. In other cases, the deactivation occurs by poisoning of the active sites by elements contained in trace amounts in the feedstock (e.g., metals, sulfur) or by the modification of the local structure of the sites themselves induced by particular reaction and/or regeneration conditions. In any case, when the performances of the catalyst drop below the limits of acceptability, it is fully replaced with a batch of fresh catalyst. The fate of the spent catalyst, in turn, depends on its characteristics and composition. If technically feasible and economically favorable, the spent catalyst is sent to the recovery of its most valuable components or conferred to industries (e.g. cement, steel factories). In less favorable cases, the spent catalyst is treated as waste and disposed of according to existing regulations, with obvious economic and environmental implications substantially related to the classification of the waste itself. The problem is certainly not negligible,

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* Corresponding author. Tel.: +39 0103536024; fax: +39 0103536028.
E-mail address: Guido.Busca@unige.it (G. Busca).

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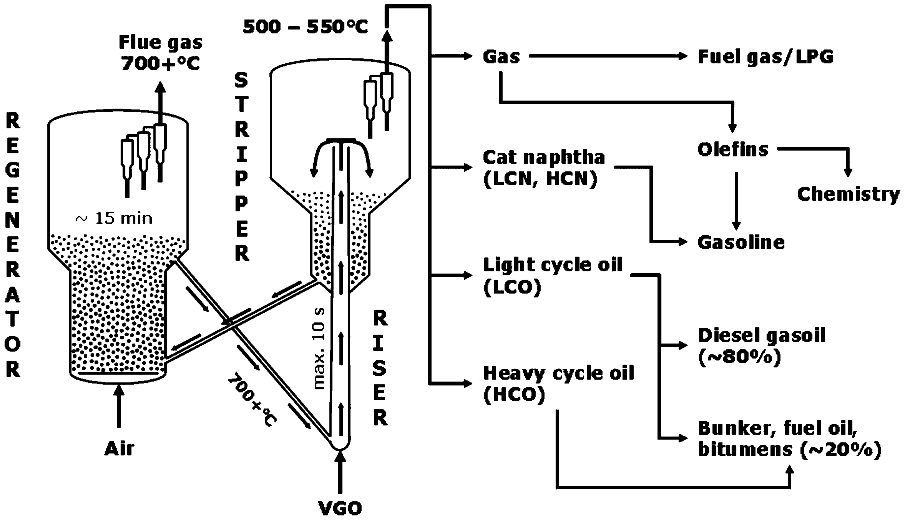

Fig. 1. Schematic representation of a FCC plant with the pool of products produced.

especially when it is considered the enormous amounts of spent catalyst that are yearly produced in the world by certain processes.

One of these is certainly the Fluid Catalytic Cracking (FCC), a key refining process employed to convert heavy oil fractions (e.g. vacuum gas-oil, VGO) into lighter products, mainly high octane gasoline and an olefin-rich gas, using a zeolite-based catalyst appropriately designed to be used in a recirculating fluidized bed reactor [2–4]. The conditions used in the FCC process are very stressful for the catalyst: during the numerous reaction-regeneration cycles, it undergoes structural modifications that, in the long run, are responsible for the loss of activity. Furthermore, a progressive accumulation of metals (in particular Ni, V and Fe contained from a few to over 250 ppmw in the crude oils [5]) takes place and this must be properly monitored to avoid the rapid degradation of the catalyst as well as the promotion of undesired reactions. Among these metals, Ni is certainly one of the most critical because, under the operating conditions, it can promote dehydrogenation reactions, which enhance the tendency of coke formation at the expenses of gasoline yield and increase the production of gas as well as of hydrogen. Moreover, the so-called "equilibrated catalysts" (ECAT's) contain, in the most common cases, 2000–5000 ppmw of Ni, and that generates also serious concerns for the disposal of the spent catalyst. In fact, a number of nickel compounds are classified as carcinogenic or toxic to reproduction, class 1A or 1B [6]. In the case of FCC catalysts, the speciation of Ni has still not been unambiguously defined. Thus, it must be supposed it to be present as NiO (nickel oxide, mineral name and bunsenite), and for this the limit of 0.1 wt% applies for the classification of the spent catalyst as hazardous wastes (Classification, Labelling and Packaging Regulation 790/2009/CE). In the absence of precise information on the speciation of Ni in spent FCC catalysts, it is difficult to assign the correct hazardous properties to the spent FCC catalyst when is disposed or recovered as a waste. Usually in such conditions, a precautionary approach, based on the assumption that the Ni is present on the catalyst in the most hazardous form (as Ni oxide or sulfides, depending on the catalyst and on the process), is adopted. Such approach induces to overestimate the real level of hazard in the waste treatment and to inappropriate disposal procedures. Just to give an idea, it was reported that a FCC plant operating in a medium-size refinery (230 kbbl d^{-1}) with a catalyst inventory of 200 t, consumes 1000 t of catalyst per year [7]. The relevance of this issue is given by the significant worldwide consumption of FCC catalyst, which in 2011 amounted to the impressive value of 627 kt [8].

To limit these effects, manufacturers have developed catalysts consisting of matrices able to bind the feed metals, reducing their undesired effects. In the case of Ni its actual state in the FCC catalyst was only occasionally discussed in the literature, especially in relation to its role in the deactivation [9–11]. The interpretations of the results obtained using different characterization techniques, however, disagree largely and no definite answers were provided about its actual state in spent FCC catalysts. In an effort to give a definitive answer to this problem, we have focused attention on the detectability of the phase responsible for the classification as hazardous of the spent FCC catalyst (NiO and bunsenite), developed on model systems an analytical procedure able to verify the limit of detection of the phase of interest and verified on a series of real spent catalyst from different refineries.

2. The FCC process and catalyst

FCC is a key technology in oil refinery because it is used to convert vacuum distillates and residues into more valuable products, mainly gasoline but even middle distillates and light olefins (e.g., propylene, butenes).

The cracking reaction is endothermic and increases the number of moles of products respect to the feed. It is therefore favored at high temperature and low pressure. The catalyst undergoes coking very rapidly and should be frequently regenerated. The FCC configuration schematized in Fig. 1 takes into account these concepts: the preheated feed (vacuum gas-oil, VGO) is fed at the bottom of the riser (the reactor) where it is mixed with the catalyst. The cracking reactions occur in the riser where the volume expansion helps the mix catalyst/feed to move upwards very rapidly (2–10 s). Then, the mix is sent to the stripper where the hydrocarbons are separated from the coked catalyst, which is finally steam-stripped from the adsorbed volatile products. The coked catalyst is finally sent to the regeneration unit, where the coke is burned off with air for 10–15 min; the regenerated catalyst, at a temperature of 700 + °C due to the exothermal combustion of coke, returns to the bottom of the riser ready for a new cycle. Fig. 1 also shows the products typically generated by FCC and their finally destination use. Whereas the relative yields depend on the characteristics of the feed (e.g. paraffinic or aromatic) and of the catalytic system, olefins, cracking naphtha and LCO are the most valuable streams. Such a complex pool of products originates from several secondary reactions (e.g. isomerization, cyclization, dehydrogenation, H-transfer),