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Nature and location of cerium in Ce-loaded Y zeolites as revealed by HRTEM and spectroscopic techniques

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Abstract

Different methods were used to introduce cerium in a HUSY zeolite. The samples obtained from ion-exchange, precipitation and wetness impregnation procedures were characterized both before and after hydrothermal deactivation in order to determine and compare the nature of the cerium species and their location in the catalyst. A variety of techniques were used: XRD, HRTEM, XPS, infrared and Raman spectroscopy and catalytic test of dehydration of 2-propanol. The presence of amorphous phases of extra framework aluminium species (EFAL) depends on the preparation method as was evidenced by TEM. The presence of CeO_2 and exchanged cerium was determined in catalysts prepared by precipitation and impregnation methods. The quantification of both types of cerium species was accomplished by Rietveld refinement. For the catalyst prepared by impregnation, it is suggested that cerium species interact with EFAL species. This interaction determines the cerium dispersion.

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1. Introduction

A subject of relevance when dealing with fluid catalytic cracking (FCC) catalysts is their stability, especially under hydrothermal treatments. These treatments are carried out periodically during the catalyst regeneration by burning off the deposited coke under a steam/air mixture at elevated temperatures. Early on, in the development of zeolitic cracking catalysts, it was found that low sodium content was required not only for an optimum activity but also as regards the hydrothermal stability [1]. Rare-earth ions, such as cerium and lanthanum are proper hydrothermal stabilizers for FCC catalysts. Nowadays, almost all zeolitic FCC catalysts are prepared by ion-exchange of rare-earth ions followed by a hydrothermal treatment, thus giving a so-called "stabilized" catalyst [2]. However, the stabilization treatment produces the dealumination of the zeolite, and extra framework aluminium species (EFAL) develop which have often been related to highly active sites [2–5].

Depending on the severity of the hydrothermal treatment, EFAL species may indeed be located on the zeolite external surface. On the other hand, at present, the processing of heavy feed stocks in the petroleum industry is increasing all over the world and in parallel, that of oil with a high content of contaminating metals (i.e. V, Ni) which poison the zeolitic FCC catalysts [6]. These metals, whether associated with sodium or not, have been described as destroying the crystalline structure of the zeolite [7–9]. This process has been associated with the metallic migration into the internal zeolitic structure during each regeneration

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step, thus shortening the active-life of the catalyst by lowering its stability. Thus, methods to passivate contaminating metals in the FCC process of hydrocarbons comprise a continuously developing area of research [10,11]. It is worth mentioning that the rare-earth elements act as metal traps and that at present, most refineries use rare-earth additives like cerium- and/or lanthanum ions as metal traps in zeolitic FCC catalysts [12,13]. Different passivation mechanisms of contaminating metals have been described. These mechanisms depend on how the rare earth component is introduced into the catalyst. It has been reported that the introduction of lanthanum and cerium via an ion-exchange technique is less efficient with respect to their incorporation by precipitation [14]. Also, we have shown that cerium introduced by the incipient wetness impregnation method prevented zeolite damage by vanadium more efficiently than did other methods, the resistance of the catalyst to hydrothermal deactivation being affected by the cerium introduction method too [15].

On the other hand, the introduction of rare-earth ions in the FCC catalysts by ionic exchange may modify their activity due to the hydrolysis of the rare earth cations or to the ionic fields inside the zeolite [16]. At this respect, in NaY zeolite exchanged with different rare-earth ions a relationship between the acidity and the radius of the rare-earth ion has been found [16,17]. For a given rare-earth ion the change on the acidity and activity may depend on the method used for its introduction.

To understand the different behaviour of cerium-containing zeolites prepared by different methods, it is necessary to know the nature and location of the cerium species in the catalyst, including the possible interaction between cerium species and EFAL species originating from the above-indicated dealumination process. The goal of this work is the characterization of cerium species in several catalysts prepared from the HUSY zeolite by exchange, precipitation or impregnation methods in order to relate both surface and structural characteristics of these materials with their catalytic behaviour. For this purpose, a combined characterization was carried out using different techniques, including transmission electron microscopy, powder X-ray diffraction, vibrational spectroscopy (FTIR and Raman), and X-ray photoelectron spectroscopy. The catalytic activity was assayed for the acid-catalyzed reaction of 2-propanol dehydration.

2. Experimental section

A NaUSY zeolite with a silicon/aluminium ratio of 13 (SAR = 13) a surface-area of 653 $m^2\,g^{-1}$ and a sodium content of 1.92 wt% was prepared according to Ref. [18]. To prepare the HUSY zeolite, the NaUSY zeolite was treated with an aqueous solution of NH_4NO_3 at 343 K, then washed, filtered, dried overnight and calcined at 873 K for 2 h. The sodium content of the resulting HUSY zeolite was lower than 0.5 % by weight. Cerium was incorporated to the HUSY zeolite by three different methods: precipitation (*n*CePP samples), incipient wetness impregnation (*n*CeIM samples), and ion exchange (*n*CeEX samples), where *n* indicates the nominal Ce % by weight in the zeolite. *n*CePP samples were prepared by addition of $CeCl_3$ and NH_3 aqueous solutions over a HUSY suspension at 363 K, keeping a pH constant value of 8. A reference sample (HUSYPP) was prepared following a similar basic treatment but without addition of the $CeCl_3$ solution. For the preparation of *n*CeIM samples, incipient wetness impregnation was performed with an ethanolic solution of $CeCl_3$ at 268 K. For comparative purposes an additional sample (2CeIM/HY) was prepared by incipient wetness impregnation over a HY zeolite (SAR = 3) prepared according to [18]. Prior to impregnation or precipitation, the HUSY zeolite was exposed to a benzene atmosphere for 1 h. Ion exchange was accomplished at 353 K with a $CeCl_3$ aqueous solution (*n*CeEX samples). Finally, all samples were dried at 373 K overnight and calcined at 873 K for 2 h. In addition, all catalysts were subjected to a hydrothermal treatment with steam at 1073 K for 3 h. The resulting samples were labeled with the *st* suffix.

Samples for transmission electron microscopy (TEM) were deposited from alcohol suspensions onto holey-carbon films supported on copper grids. The instrument was a Philips CM30 electron microscope operating at 300 kV and equipped with a LaB6 electron source. Point-to-point resolution was 1.9 Å.

X-ray diffraction experiments (XRD) were performed in a Bragg–Brentam $\theta/2\theta$ Siemens D-500 diffractrometer using a Cu source working at 40 kV and 30 mA. The Cu Kα wavelength was selected by means of a secondary graphite monochromator. A scintillation NaI(Tl) detector was employed. In addition to standard routine scans at 2θ from 4° to 70°, Rietveld refinements were carried out on samples mixed with α-Al_2O_3 (20 wt/wt%) by measuring 2θ from 3° to 81° with a step size of 0.03° and 19 s per step as measuring time.

Infrared spectra were obtained at room temperature with a Nicolet 520 Fourier Transform spectrometer by collecting 128 scans at a resolution of 4 cm^{-1}. Before the measurements, the samples were treated under vacuum at 473 for 14 h and then at 673 K for 4 h.

Raman spectra were recorded with a Jobin Yvon T64000 instrument using an Ar ion laser as an illumination source (514.5 nm) and a CCD detector cooled at 140 K. The laser power at the samples was kept at 2.0 W. The acquisition time was less than 20 s. The spectral resolution was estimated to be better than 2 cm^{-1}.

The X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R instrument equipped with a Mg Kα source (1253.6 eV), a hemispherical analyzer and a pre-treatment chamber. The binding energies (±0.1 eV) were referenced to the C1s peak at 284.9 eV due to adventitious carbon. The powder samples pressed in 8 mm diameter copper troughs were fixed on the XYZ manipulator. The base pressure in the analysis chamber was maintained below 4×10^{-9} mbar during data acquisition. The area

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