



Structure and acidity of individual Fluid Catalytic Cracking catalyst particles studied by synchrotron-based infrared micro-spectroscopy

Inge L.C. Buurmans¹, Fouad Soulimani¹, Javier Ruiz-Martínez, Hendrik E. van der Bij, Bert M. Weckhuysen*

Inorganic Chemistry and Catalysis Group, Debye Institute for NanoMaterials Science, Faculty of Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

ARTICLE INFO

Article history:

Available online 17 August 2012

Keywords:

Fluid Catalytic Cracking
Infrared microscopy
Zeolites
Deactivation
Acidity

ABSTRACT

A synchrotron-based infrared micro-spectroscopy study has been conducted to investigate the structure as well as the Brønsted and Lewis acidity of Fluid Catalytic Cracking (FCC) catalyst particles at the individual particle level. Both fresh and laboratory-deactivated catalyst particles have been studied. The applied deactivation protocols were steaming (ST), two-step cyclic deactivation (CD) and Mitchell impregnation-steam deactivation (MI). In addition, an equilibrium catalyst (Ecat) taken from a real cracking unit has been investigated. From the infrared spectra of the fresh and laboratory-deactivated samples it was clear that the zeolite component experiences partial collapse upon deactivation. Furthermore, it was found that characteristic bands, caused by the presence of clay material, are lost upon deactivation. After pyridine adsorption, the acidity of the samples could be monitored. Both Brønsted and Lewis acidity decreased in the following order: Fresh > ST > CD > MI. The Ecat sample was found to display acidity in between those of CD and MI samples. These findings are in line with earlier bulk transmission infrared as well as ammonia temperature programmed desorption measurements, which confirms the validity of acidity measurements at the single particle level. However, additional information about the distribution of Brønsted and Lewis acidity within individual catalyst particles becomes available. The developed approach reveals a larger variety in the amount of Brønsted acid sites for individual Ecat particles as compared to CD and MI particles. This observation can be attributed to the wide age distribution within industrial equilibrium catalysts and directly shows the added value of micro-spectroscopy approaches in the investigation of interparticle heterogeneities.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The study of acidity and reactivity of microporous and mesoporous catalytic materials, such as zeolites, has been a topic of interest since many years. In industry such catalyst materials are used in a wide variety of processes, among which oil refining, petrochemistry and organic synthesis [1]. A large range of bulk techniques for the characterization of acidity in solid materials is available [2–6]. Some important examples of such methods are temperature programmed desorption (TPD) of basic probe molecules, e.g. ammonia [7,8] or amines [9], activity analysis in hydrocarbon cracking [10,11], solid-state NMR spectroscopy [12] and IR spectroscopy in combination with various probe molecules [13–15]. By the application of pyridine, lutidine and collidine, basic probe molecules of different molecular sizes, an accessibility index of the different types of acid sites within zeolite materials was obtained [15].

An interesting development in the field of catalysis research is the application of micro-spectroscopic techniques, which allow the investigation of catalyst materials and catalytic reactions in a space-resolved manner [16–22]. By applying these approaches, new insights into the reactivity and structure of catalytic materials at the single particle level can be obtained [23–27]. A very useful development for the investigation of Brønsted and Lewis acidity in catalytic materials is the application of synchrotron-based IR micro-spectroscopy in combination with pyridine adsorption. Pyridine adsorption is frequently used for acidity studies since the interaction with both types of acid sites gives rise to different C–C stretch vibration frequencies [28,29]. IR light from a synchrotron source is about 100–1000 times brighter compared to a conventional IR source, thus allowing the use of a smaller aperture in order to obtain spatial information of the catalyst samples under investigation [30–32]. Furthermore, the brightness of the IR light is sufficient to enable measurements in transmission mode, which facilitates the investigation of the acidity of the whole internal volume of catalyst bodies, instead of obtaining only information about the acidity of the external surface of such materials.

In the research described here, the structure and acidity of Fluid Catalytic Cracking (FCC) catalyst particles, used in industry for the

* Corresponding author. Tel.: +31 302537400; fax: +31 302511027.

E-mail address: b.m.weckhuysen@uu.nl (B.M. Weckhuysen).

¹ These authors contributed equally to this work.

production of transportation fuels and other hydrocarbons from crude oil fractions [33–36], is examined using synchrotron-based IR micro-spectroscopy. The catalyst for the FCC process consists of spray-dried porous microspheres with an average diameter of 70 μm that are complex mixtures of several materials. Typically the catalyst particles contain 20–40% ultrastable Y zeolite (USY) and a matrix, consisting of a clay component, silica and alumina. Zeolite Y is able to crack the alkanes and alkylaromatics in oil feed, as well as intermediates that are pre-cracked by the matrix materials. Acid-catalyzed pathways are assumed to be the main cracking routes during the process. For that reason, the Brønsted acidity of the FCC components influences the overall cracking activity of the catalyst.

During cracking reactions, several factors influence the acidity and the activity of the catalyst particles. The most important deactivating factors are exposure to steam [37], coke formation [35,37,38] and metal deposition [39]. Steam is applied in the so-called stripper of the FCC reactor to remove adsorbed product molecules from the catalyst. This steam, especially in combination with the high temperatures in the reactor, can cause partial dealumination of the zeolite component and destruction of a part of the microporous zeolitic structure. Secondly, the deposition of coke species, aromatic carbonaceous molecules, within the catalyst bodies blocks their accessibility and thus reactivity towards new cracking reactions. In an industrial FCC unit this coke is burnt off in the regenerator to restore some of the initial catalytic activity. During this combustion more steam is generated, which causes further degradation of the zeolitic component. Another very important deactivating factor in the FCC process is the presence of metal ions in the oil feed. Especially nickel and vanadium, mostly found as metal porphyrins in crude oil [40], favor dehydrogenation reactions and thus coke formation. Furthermore, vanadium species can damage the zeolite structure, leading to a loss of active surface area [37,41].

A variety of laboratory deactivation methods has been developed to simulate the influence of hydrothermal conditions, coke formation and metal deposition on the activity and structure of FCC catalyst particles. The three deactivation protocols explored in this article are steaming (ST) [42], two-step cyclic deactivation (CD) [43–47] and Mitchell impregnation-steam deactivation (MI) [48]. After regeneration in a real FCC unit the catalyst can be re-used, but during every cycle some catalyst is lost due to attrition and degradation of the particles. To maintain a stable conversion level, an amount of fresh catalyst is added to the FCC unit after each cracking–stripping–regeneration round. This addition leads to a mixture of catalyst particles with a broad age distribution in the FCC unit and as a consequence also large heterogeneities in properties are observed when comparing individual catalyst particles and their performance [36,49]. The mixture that is present in a real FCC unit is for that reason called an equilibrium catalyst (Ecat) and it is expected that the age distribution within such an Ecat is also reflected in its acidity properties.

The aim of this paper is to study with synchrotron-based IR micro-spectroscopy the structure and acidity of individual fresh and ST, CD and MI laboratory-deactivated catalysts as well as an Ecat sample at the single particle level. In this manner, new physicochemical information becomes available on *interparticle* heterogeneities taking place during the deactivation of industrially relevant FCC catalyst materials.

2. Experimental

Pyridine (Acros Organics, 99+%, for spectroscopy) was used as received. FCC catalyst particles and their separate components were provided by Albemarle Corporation and used as received.

Only the two-step cyclic deactivated (CD) and Ecat sample were calcined before use at 973 K for 2 h. Pyridine adsorption on the FCC catalyst particles was performed by heating 0.5 g of catalyst in a round bottom flask under vacuum (10^{-3} mbar) at 573 K for 2 h. Subsequently, 0.6 mL of pyridine was added to the catalyst through a septum. After pyridine addition the samples were dried at room temperature in air for 3 h, after which excess pyridine was removed by heating at 363 K for 15 min. Subsequently, the FCC catalyst particles were used for the IR micro-spectroscopy and bulk IR experiments under ambient conditions in air.

Deactivation of FCC catalyst particles was performed by Albemarle Corporation using three different methods, namely steaming (ST); 2-step cyclic deactivation (CD) and Mitchell impregnation-steam deactivation (MI). Deactivation of fresh FCC catalyst particles by three different methods was preceded in all cases by sieving (between 38 and 125 μm). Steam deactivation occurred by first preheating/drying in air to 873 K for 1 h followed by treatment at 1061 K for 20 h in 100% steam. Mitchell impregnation-steam deactivation [48] is a two-part method: First, incipient wetness impregnation of metal naphthenates dissolved in hexane (7500 ppmwt atomic Ni, 3000 ppmwt atomic V as measured by XRF on catalyst) was performed. Subsequently the samples were dried in air, after which a multistep calcination was performed, heating in air (2 h each at 473, 673 and 873 K). Secondly, a steam deactivation, as described for the steam deactivation method, was performed for 10 h. Two-step cyclic deactivation was performed on an Imtech Cyclic Deactivation unit with 20 cycles of alternating cracking–regeneration (step 1) followed by 120 cycles of alternating oxidation–reduction (step 2) to achieve 7500 ppmwt Ni and 3000 ppmwt V on the catalyst. Each sieved catalyst was preheated/dried to 873 K for 1 h prior to loading in the CD unit. A single cycle in step 1 consisted of fluidizing the catalyst in N_2 to crack a vacuum gas oil spiked with metal naphthenates at 773 K for 5 min, stripping hydrocarbons from the catalyst pores with N_2 for ~ 7 min while heating from 773 to 923 K, and regenerating the catalyst at 923 K for 30 min in a O_2/N_2 mixture (40:60 mol%). A single cycle in step 2, conducted continuously at 1043 K in steam, consisted of oxidation in $\text{H}_2\text{O}/\text{O}_2/\text{N}_2$ (40:25:35 mol%) for 2 min, stripping in $\text{H}_2\text{O}/\text{N}_2$ (40:60 mol%) for 1.5 min, reduction in $\text{H}_2\text{O}/\text{H}_2/\text{N}_2$ (40:25:35 mol%) for 7 min, and stripping in $\text{H}_2\text{O}/\text{N}_2$ (40:60 mol%) for 1.5 min. Temperatures in the CD unit were measured in the fluidized catalyst bed by a thermocouple.

Fourier transform infrared (FT-IR) microscopy experiments of individual catalyst particles were performed at beamline U10B at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (Upton, NY, USA). A Thermo Nicolet Continuum IR microscope with a $32\times$ Schwarzschild objective, connected to a Thermo Nicolet Magna 860 FTIR spectrometer equipped with an MCT-detector was used. Synchrotron-based IR light was used as the infrared light source. The FCC catalyst particles with and without adsorbed pyridine were, without any further treatment, placed on a 1 mm thick CaF_2 slide and IR spectra were collected in transmission mode in the $4000\text{--}1000\text{ cm}^{-1}$ wavenumber range with a spectral resolution of 4 cm^{-1} . An IR beam (aperture) size of $20\times 20\text{ }\mu\text{m}$ was used and 128 scans per spectrum were taken. The average particle size of all particles under study was 75 μm .

Bulk transmission IR experiments were performed on self-supported catalyst wafers of ground FCC catalyst particles (20 mg) after pyridine adsorption, which were pressed at a pressure of 5 ton cm^{-2} applied for 3 min. The catalyst wafers were placed inside a holder for transmission IR measurements. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR instrument. For each spectrum 128 scans were recorded with 4 cm^{-1} resolution. Bulk transmission IR spectra of the separate FCC components (i.e., zeolite Y with Si/Al ratios of 3.5, 5.5, 15 and 27.5; clay; silica and low-crystalline alumina) were recorded both before and after

Download English Version:

<https://daneshyari.com/en/article/6533722>

Download Persian Version:

<https://daneshyari.com/article/6533722>

[Daneshyari.com](https://daneshyari.com)