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Measurements and distinguishment of mass transfer processes in fluid catalytic cracking catalyst particles by uptake and frequency response methods

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ABSTRACT

The mass transfer processes in REUSY zeolites and fluid catalytic cracking (FCC) catalyst particles have been measured and distinguished in this study by uptake method with an intelligent gravimetric analyser (IGA) and by the frequency response (FR) technique. The results indicate that the diffusion time constants in the FCC catalyst particles are smaller than those in the REUSY zeolites, and the limiting steps for the overall mass transfer processes in the FCC catalyst particles are the diffusion process in the length scale of macropore of the matrix or/and the mass transfer at the zeolite–matrix interface rather than the intracrystalline diffusion one in the micropores of the zeolite crystals.

1. Introduction

FCC catalysts particles are typical hierarchical porous materials, containing a complex system of micro-, meso- and macropores located in the zeolites and the matrix, in which different modes of mass transfer processes are expected, such as adsorption and diffusion in the micropores of the zeolite crystals, the mass transfer of molecules at the zeolite–matrix interface, diffusion in the meso- and macropores of the matrix, and the molecular exchange at the matrix–vapor interface, etc. While it is expected that the effective diffusion coefficient, D_e, in the zeolite component is smaller than that in the matrix component, the particle radius, r, of the zeolite crystallite is about one hundred times smaller than that of the overall FCC catalyst particle. Because the overall rate of transport depends on the diffusion time constant, D/r^2, for each component present, it is therefore important to see whether the limiting step for molecular transport in FCC catalyst particles occurs in the matrix or zeolite component. This knowledge is very useful not only in the catalyst optimization, but also in the design of the riser and the stripper.

Few published studies on the mass transfer processes in commercial FCC catalysts can be, however, searched due to the complexity of the systems and the lack of suitable experimental methods [1–5]. Barrie and coworkers [2] reported pioneering work in which the Tapered Element Oscillating Microbalance (TEOM) technique was employed to identify the limiting step from the transport processes in FCC catalysts. It was proposed that the rates of adsorption and desorption of the hydrocarbons studied are the same for the FCC catalyst as that for the pure zeolite Y sample, suggesting that the mass transport in the matrix component of the FCC catalyst is a rapid process in the system. They also numerically simulated the TEOM results which can be fitted well only when the particle boundary transport at the zeolite–vapor and zeolite–matrix interfaces is considered as the limiting step affecting the adsorption kinetics [3]. It was, therefore, suggested that, for the FCC catalyst, the limiting step is the transfer of molecules at the zeolite–matrix interface. Utilizing the pulsed-field gradient nuclear magnetic resonance (PFG NMR) technique, Kärger group in Leipzig

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University [4] measured the diffusion processes in FCC catalysts on various displacement scales. It turned out that the limiting rate is primarily related to the diffusion mode associated with displacements larger than the size of zeolite crystals but smaller than the size of the particles.

Sedran and coworkers [5] reported the diffusion and adsorption selectivities of hydrocarbons over FCC catalysts using a CREC Riser Simulator laboratory reactor. In this study, system evolution was modeled by Fick's 2nd law on the assumption that (i) mass transfer and adsorption in the matrix component of the FCC catalyst particle are negligible in comparison with those in the zeolite component and that (ii) local adsorption equilibrium with the gas phase is instantaneously attained at the surface of the zeolite particles, following a Langmuir-type isotherm. The conclusions from their studies were queried as the results contradict to the evidence of direct diffusion measurements by the PFG NMR technique [6–9].

As mentioned above, a consensus mechanism of mass transfer processes in FCC catalysts has not been achieved for such complicated system and more detailed measurements for direct detection of the mass transfer processes occurring simultaneously in FCC catalysts are needed still.

The FR technique has proved to be a very effective and a very powerful method for determining inter- and intracrystalline diffusivities of sorbate molecules in zeolites [10–12]. Diffusion coefficients in the micropores of different zeolite/adsorbate systems obtained by the FR technique have been found to agree closely with pulsed-field gradient (PFG) NMR results [13]. An outstanding advantage of the FR method is its ability to distinguish multi-kinetic processes in an FR spectrum, i.e. various 'independent' rate processes which occur simultaneously can be investigated by this technique [14]. This method can also be used to characterize the acid sites present in zeolite catalysts using ammonia as the probe molecule at catalytic temperatures and metal aggregates in bifunctional zeolite catalysts using oxygen and hydrogen as the probe molecules.

In this paper, the adsorption dynamics properties and mass transfer behavior of guest molecules of thiophene, benzene, *p*-xylene, cumene, and *n*-octane in some FCC catalysts and REUSY zeolites have been studied by using the IGA and the FR techniques, by which multi-kinetic processes can be characterized and distinguished, to provide a better understanding of mass transfer processes in FCC catalyst particles.

The present work mainly focus on mass transfer properties in FCC catalyst particles, all the measurements were, therefore, carried out at temperatures much lower than those typically used in FCC units to exclude the chemical reactions. It is not easy to operate the measurements for the probe molecules heavier than C_8 due to the very low saturated vapor pressure. Great difficulties have been encountered during the experiments even with *n*-octane. Smaller molecules are, however, efficient for the above purpose.

Thiophene is used as a probe molecule for the fact that the molecule configurations of thiophene and benzene are similar, so the diffusion behavior of the two compounds should be analogous in the catalysts. The adsorption properties of these two molecules are, however, quite different in the catalysts especially in the acidic zeolites. Compared to benzene, thiophene is much stronger adsorbed. Also thiophene is much more active than benzene in the acidic zeolites and the oligomerization of thiophene may occur in the zeolites which will block the pore mouth of the micropores in the zeolite crystals. These adsorption properties of thiophene on the zeolites are skillful to eliminate the zeolite–matrix interface resistance to the macropore diffusion. By comparing the experimental results of benzene and thiophene, it would be, therefore, effective to investigate the presence of the zeolite–matrix interface resistance.

2. Experimental

2.1. Materials

Commercial FCC catalysts (LDO-70 and LDO-70S) and REUSY zeolites (HRSY-1 and HRSY-3) were provided by Petrochemical Research Institute, China National Petroleum Corporation. The catalyst particles, with a mean size of ca. 70 μm, studied in the present work contain the same fractions of the same industrial REY zeolite only with different additives (one more additive for LDO-70S than LDO-70) used. SEM images show that the mean size of the zeolite crystals for both the zeolite samples containing different contents of RE species (HRSY-1 < HRSY-3) is ca. 0.5 μm. All the catalysts and zeolites were not deactivated prior to the measurements.

The adsorbates of benzene, *p*-xylene, cumene, *n*-octane, and thiophene (GC standard, >99.96%, J&K Chemical) were used without further purification.

2.2. Texture characterizations

N_2 adsorption isotherms were measured by using a Micromeritics ASAP 2020 at −196 °C. The samples (ca. 0.15 g) were in situ degassed under a vacuum of $<10^{-3}$ Pa at 300 °C for 4 h prior to analysis.

2.3. Adsorption and uptake measurements

Gravimetric sorption isotherms and uptake rate measurements were obtained by the IGA instrument, model IGA-003, Hiden Analytical Ltd., Warrington, UK. The sensitivity of the balance is 1 μg. The buoyancy correction following from Archimede's principle is considered to yield the true weight. Pressure is controlled via the use of three transducers with ranges of 0–0.002, 0–0.2 and 0–10 bar, with an accuracy of 0.02% of the specified range. The temperature uncertainty and stability are 0.1 and 0.05 °C, respectively, which is regulated with a water bath or a heating furnace outside the reactor.

The samples for the Gravimetric sorption isotherms and uptake rate measurements were prepared as follows. Approximative 450 mg of the FCC catalysts and 150 mg of the REUSY zeolites were introduced into the sample container connected to a vacuum system and the samples were degassed under a vacuum of $< 10^{-3}$ Pa at 400 °C for 10 h. The adsorbate gases used were subjected to several freeze-pump–thaw cycles for purification before connected to the measured adsorbents.

The adsorption isotherms were measured by increasing (for adsorption) or decreasing (for desorption) the equilibrium pressure step by step. The real-time uptake data were recorded for each equilibrium pressure.

2.4. Frequency response measurements

The frequency response setup is a high vacuum ($<10^{-3}$ Pa) unit equipped with a volume modulation part, consisting a magnetically driven plate sealed with two ultra-high vacuum bellows. The volume of the adsorbate–adsorbent system was modulated by a square-wave perturbation of ±1% over a range of frequencies of 0.01 to 10 Hz. The pressure changes response to the volume perturbations were measured by a high-accuracy differential Baratron pressure transducer (MKS 698A11TRC). The frequencies were controlled by an on-line computer, which was also used for the acquisition of the pressure data from the Baratron.

Accurately known amount of zeolite samples (ca. 50 mg) were scattered in a plug of glass wool and degassed under a high vacuum of $< 10^{-3}$ Pa at 400 °C for 10 h. Prior to the measurement the sorbate vapor from the supply side of the vapor reservoir was admitted to the sorption chamber and equilibrated over the sample at a