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Catalytic cracking performance of alkaline-treated zeolite Beta in the terms of acid sites properties and their accessibility

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ABSTRACT

The zeolite Beta is considered as a promising additive for FCC catalyst in diesel oil production. In this article, it is shown that hierarchical zeolite Beta obtained by an optimized desilication procedure increases diesel and propylene yields during gas–oil cracking reaction. The alkaline treatment of zeolite Beta (Si/Al = 22) by desilication with NaOH and NaOH&TBAOH was investigated. The catalytic performance improvement of desilicated zeolite Beta has been rationalized by deep characterization of the samples including X-ray diffraction, low-temperature adsorption of nitrogen, solid-state ^{29}Si MAS NMR and IR studies of acidity. Finally, the catalytic performance of the zeolites Beta was evaluated in the cracking of *n*-decane, 1,3,5-tri-iso-propylbenzene, and vacuum gas oil. It was found that desilication with NaOH&TBAOH ensures the more uniform intracrystalline mesoporosity with the formation of narrower mesopores, while preserving full crystallinity resulting in catalysts with the most appropriated acidity and then with better catalytic performance.

1. Introduction

Zeolites are well-known catalysts of high surface area, high hydrothermal and thermal stability, structural pores of molecular dimensions, and hosting strong Brønsted and Lewis acid sites. These unique properties are responsible for their application as catalysts in many major chemical processes [1,2]. The main advantages of the micropores of molecular dimensions are their extremely high surface area and shape selectivity. However, also diffusional limitations are frequently observed when large molecules are processed, which induce fast catalyst deactivation [3]. To improve the catalyst effectiveness in chemical reactions, desilication i.e. controlled silicon extraction from the zeolite framework in alkaline aqueous solution has been developed as one of the most efficient methods to design micro- and mesoporous (hierarchical) zeolites [4,5]. The desired intracrystalline mesoporosity is ruled by the interplay of micro- and mesopores and is, however, influenced by the value of the framework Si/Al ratio [6,7]. It has been reported that aluminium atoms in framework positions play a crucial role in silicon extraction directing the mesopore formation process, as the AlO_4^- tetrahedra are reported to protect Si atoms in the neighbourhood against OH^- ions attack due to electrical repulsion [8]. Alkaline leaching, performed in aqueous NaOH and tetraalkylammonium hydroxides mixtures, leads to the dissolution of both Si and smaller amounts of Al species from the framework. Nevertheless, most of these extracted Al species are able to realuminate on the mesopore surface, resulting in lowering the Si/Al ratio of the hierarchical [9,10]. Zeolite desilication has been successfully applied to produce a large number of hierarchically structured zeolites MFI [11,12] MTW [13], MOR [14,15], FER [16,17], FAU [18], and Beta [19,20]. Nevertheless, the benefits of desilicated zeolite Beta for catalytic cracking reaction have not been shown in previous studies.

Zeolite Beta belongs to a complex family, consisting in intergrowth of two polymorphs (polymorph A and B) [21,22] and it is characterized by a 3D channel system formed by micropores limited by 12-MR windows (ca. 0.7 nm in diameter). The remarkably lower stability of zeolite Beta structure during desilication in comparison with ZSM-5 and mordenite has been reported [20]. Also, the influence of framework aluminium content for controlled desilication was shown [8]. Therefore, it can be assumed that the low stability of Al atoms in the framework positions in zeolite Beta [23], caused by the presence of high concentration of structural defects [24], can also affect the desilication process and the high amount of EFAL species can be detected. Framework silicon

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extraction from zeolite Beta (Si/Al = 220) upon treatment with NaOH revealed the extensive mesopore formation of intracrystalline nature; meanwhile, the micropore volume and crystallinity of the desilicated materials was severely reduced [19]. This clearly show that basic treatments, even at mild conditions, destructively affect the structural and acidic properties of zeolite Beta, contrarily to that observed on MFI, MOR and MTW [11,12].

The application of desilicated hierarchical large pore zeolites for gasoil cracking has been recently studied for zeolite USY [25] and mordenite [26]. In these studies, the mesoporosity enhancement increases the yield of middle distillates, while preserving or even increasing overall catalytic activity and olefinicity in C_3—C_4 gas fraction. Zeolite Beta has been considered as an alternative to ZSM-5 as potential additive for the USY-based FCC catalyst for increasing C_3—C_4 olefins with low penalty in the yield of gasoline [27–29]. However, the commercial use of zeolite Beta as FCC additive is limited due to its faster deactivation when compared to ZSM-5.

In this work, we describe first study of the applicability of hierarchical zeolite Beta for industrially relevant gas–oil cracking reaction. The catalytic performance, including gas oil, *n*-decane and TIPB cracking on hierarchical zeolites Beta has been explained on the basis of their textural and acidic properties. We demonstrate that an optimized desilication procedure able to produce well-controlled mesoporosity in zeolite Beta improves the catalytic performance, increasing its overall gas–oil cracking activity with high yields to propylene and middle distillates and lower coke production.

2. Experimental

2.1. Catalyst preparation

The parent zeolite NH_4Beta of Si/Al = 22 was purchased from Zeolyst (CP814C). Desilication was carried out in the 0.2 M solutions of NaOH and NaOH&TBAOH (tetrabutylammonium hydroxide) mixture (TBAOH/(NaOH + TBAOH) = 0.4) at the temperature of 65 °C for 0.5 h. After desilication, the suspension was cooled down in ice-bath, filtered, and washed with distillate water until neutral pH. Next fourfold Na^+/NH_4^+ ion-exchange with 0.5 M NH_4NO_3 was performed at 60 °C for 1 h. Finally, the resulting samples were again filtrated, washed, and dried at room temperature.

2.2. Characterization methods

The powder X-ray diffraction (XRD) measurements were carried out using a PANalytical Cubix X'Pert Pro diffractometer, with Cu Kα radiation, λ = 1.5418 Å in the 2θ angle range of 2–40°. Powder X-ray patterns were used for structural identification of the relative crystallinity value (%Cryst) for all the zeolites. The determination of the relative crystallinity value was based on the intensity of the characteristic peaks in the range between 20.0° and 24.0°.

Si and Al content in the parent and desilicated zeolites was determined by ICP OES spectroscopy on an Optima 2100DV (PerkinElmer) instrument.

The X-ray photoelectron spectra (XPS) were measured on a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyser. The photoelectron spectra were measured using a monochromatized aluminium Al Kα source (E = 1486.6 eV) and a low-energy electron flood gun (FS40A-PS) to compensate the charge on the surface of nonconductive samples. The base pressure in the analysis chamber during the measurements was 5×10^{-9} mbar. Spectra were recorded with constant pass energy of 100 eV for the survey and for high-resolution spectra. The binding energies were referenced to the Si 2p core level (103.0 eV). The composition and chemical surrounding of the sample surface were investigated on the basis of the areas and binding energies of Al 2p, Si 2p and O 1s photoelectron peaks. The fitting of high-resolution spectra was provided through the CasaXPS software.

The solid-state MAS NMR spectra were acquired on an APOLLO console (Tecmag) at the magnetic field of 7.05 T (Magnex). For the ^{29}Si MAS NMR spectra, a 3 μs rf pulse ($\pi/2$ flipping angle) was used, 4 kHz spinning speed, and 256 scans with the delay of 40 s were acquired. The ^{27}Al spectra were recorded using the 2 μsrf pulse ($\pi/6$ flipping angle), 8 kHz spinning speed, and 1000 scans with acquisition delay 1 s. The frequency scales in ppm were referenced to TMS and to 1 M solution of $Al(NO_3)_3$, for the ^{29}Si and ^{27}Al spectra, respectively. The spectra were normalized to the mass of sample.

The N_2 sorption processes at −196 °C were studied on an ASAP 2420 Micromeritics after activation in vacuum at 400 °C for 12 h. Surface Area (S_{BET}) and micropore volume (V_{micro}) were determined by applying the BET and *t*-plot methods, respectively. Pore size distribution and volume of mesopores (V_{meso}) were obtained by applying the BJH model to the adsorption branch of the isotherm.

The QE-TPDA measurements of *n*-hexane and *n*-nonane were performed with use of the flow TPD system equipped with thermal conductivity detector (Micro Volume TCD, Valco) presented more into detail earlier [30,31]. Prior each measurement, a sample (ca. 10 mg) was activated by heating in He flow (10 °C/min to 500 °C). Adsorption was carried out at room temperature by replacing pure helium used as the carrier gas with helium containing small concentration of hydrocarbon (ca 0.4 vol%). After completed adsorption, the QE-TPDA experiment was performed by cyclic heating and cooling the sample (2 or 10 °C/min up to 500 °C) in He/HC flow (6.5 cm^3/min). Desorption–adsorption cycles were separated with 1 h isothermal segments at room temperature. In the micro- and mesopore volume calculations, the experimental desorption maxima were integrated and related to the calibration data. Density of the adsorptive was assumed as equal to that of the liquid.

For FTIR studies, the samples were pressed into the form of self-supporting discs (ca. 5 mg/cm^2) and evacuated in a quartz IR cell at 530 °C under vacuum for 1 h. Spectra were recorded with a Bruker Equinox 55 spectrometer equipped with a MCT detector. The spectral resolution was of 2 cm^{-1}. The CO adsorption was performed at −100 °C. Pyridine (Py) was adsorbed at 170 °C, the concentration of Brønsted and Lewis acid sites determined in quantitative IR studies of pyridine adsorption, according to the procedure given in Ref. [32]. The values of 0.10 cm^2/μmol and 0.07 cm^2/μmol were obtained for the 1450 cm^{-1} band of pyridine coordinatively bonded to Lewis sites (PyL) and for the 1545 cm^{-1} band of pyridinium ion (PyH^+), respectively. The ammonia adsorption experiments were performed according to following procedure. An excess of ammonia, sufficient to neutralize all the acid sites, was adsorbed at 130 °C [33] and the physisorbed molecules were removed by evacuation at the same temperature. The concentration of Brønsted and Lewis sites was calculated from the intensities of 1450 cm^{-1} and 1620 cm^{-1} bands of ammonium ions (NH_4^+) and ammonia interacting with Lewis sites (NH_3L) and their extinction coefficients. The extinction coefficient of NH_4^+ 1450 cm^{-1} band was determined as a slope of the linear dependence of the intensity of this band versus the amount of ammonia adsorbed in zeolite NaHY containing only protonic sites (the value 0.11 cm^2/μmol was obtained). The extinction coefficient of NH_3L band was determined in the experiments in which ammonia was sorbed in zeolite HY dehydroxylated at 800 °C containing practically only Lewis acid sites. The value of extinction coefficient was calculated from the linear dependence of 1620 cm^{-1} band versus the amount of ammonia interacting with Lewis sites (the amount of ammonia sorbed