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Texture, acidity and fluid catalytic cracking performance of hierarchical faujasite zeolite prepared by an amphiphilic organosilane

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ABSTRACT

Mesoporous zeolite Y was synthesized by using an amphiphilic organosilane. The texture and acidity of the mesoporous zeolite samples were compared with a reference microporous faujasite zeolite. The synthesis of the most suitable mesoporous zeolite Y was scaled up in order to prepare composite catalysts that could be tested for fluid catalytic cracking. Composite catalysts were prepared by spray-drying the zeolite with kaolin as filler and an alumina sol as binder. The acidic properties of composite FCC catalysts prepared from conventional and mesoporous faujasite zeolites were compared. While IR spectroscopy after H/D exchange with deuterated benzene indicates that strong bridging hydroxyl groups are present in the freshly prepared composite catalysts, these zeolite-type acid sites are absent in the lab-deactivated composite catalysts. These samples contain a significant number of weaker Brønsted acid sites. The strength of the acid sites in the composite catalysts is comparable with the acidity of amorphous silica–alumina. The composite catalysts show an excellent catalytic performance in the fluid catalytic cracking of vacuum gas oil. Our data indicate that relatively weak acid sites catalyze the FCC reactions. The well-embedded mesoporosity in the parent hierarchical zeolite crystals results in increased diesel and decreased gasoline and coke yield in the composite FCC catalyst.

1. Introduction

Fluidized catalytic cracking (FCC) is one of the key processes in the refinery industry, converting heavy gas oils obtained from atmospheric and vacuum distillation into lighter products [1–4]. The products from FCC units are valuable for the gasoline and diesel pool. Currently, more than 400 FCC units are operated worldwide, converting approximately 10 million barrels of heavy feedstock per day [1]. The success of this process is based on its simplicity, relatively low construction and operation costs and the flexibility in processing various types of heavy feedstock [4]. Zeolite Y has been the main acid component of FCC catalysts. Composite FCC catalysts used in industry further comprise clays, binders and other additives [5]. Zeolite Y is the preferred zeolite component because of its relatively large pore openings (7.4 Å), strong Brønsted acidity and good (hydro)thermal stability [6,7]. Another important aspect is that it can be synthesized at low cost without organic structure-directing agents.

Under FCC conditions, the pore openings of 7.4 Å impose diffusion limitations and limit the conversion of the larger hydrocarbon molecules in the feed. One approach to overcome this would be to prepare zeolites with larger pores, but such zeolites are usually not very stable and their synthesis requires expensive organic templates [8–11]. Another approach to ease diffusion of large molecules in zeolites is the fabrication of hierarchical zeolites that contain mesopores well-interconnected with the micropore network in the zeolite [12–14]. One distinguishes bottom-up and top-down approaches. In top-down approaches, usually Si [15–18] or Al [19–24] atoms are extracted from the zeolite framework. In bottom-up approaches, the mesoporous zeolite is formed in one step, usually by adding to the synthesis gel a second template as void filling spheres such as carbon black particles or in the form of organic molecules that act as mesoporogen during the formation of the zeolite [24].

Hierarchization has most frequently been applied in the synthesis of ZSM-5 and BEA zeolites [12,14,24,25]. It is well-known that mesopores are created in zeolite Y crystals during steam treatment as employed to convert low-acidic freshly prepared zeolite Y into strongly acidic ultrastabilized Y zeolites, which are the main acid component in hydrocracking operations [18]. Usually, the mesopores are not uniformly distributed over the zeolite crystals and, sometimes, they are also not connected to the external surface [26]. De Jong and co-workers investigated how steam treatment followed by acid and base leaching steps improves the mesopore interconnectivity, which is useful to limit secondary cracking reactions [27]. The benefit of mesoporosity on the cracking performance of vacuum gas oil and bulky model molecules has been well established [28–32].

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Mesoporous Y zeolite can also be obtained using surfactant templates [33–40]. Garcia-Martinez et al. reported about the scale-up of a surfactant-templated process to prepare mesoporous Y zeolite; composite catalysts based on such hierarchical zeolite Y showed improved yield of valuable gasoline and light cycle oil (LCO) products over bottoms and coke in FCC catalyst evaluation [41]. Another versatile method to introduce mesopores in zeolites involves the use of organosilanes that covalently bind to the growing zeolite surface [33–37]. This approach was first described by the Ryoo group in the preparation of mesoporous ZSM-5 [33]. The organosilane dimethyloctadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC) has also been used in the preparation of hierarchical zeolite Y [34–36]. For instance, Fu et al. reported improved catalytic performance in the hydrodesulfurization of 4,6-dimethyldibenzothiophene using a TPOAC-templated mesoporous Y zeolite support [34]. Another example is the benefit of mesopores in zeolite Y in the aldol condensation of n-butanol with benzaldehyde [35]. Jin et al. showed that replacing a small portion of bulk zeolite Y with hierarchical zeolite Y led to a shift in the FCC selectivity from coke to gasoline and dry gas products [36].

In the present study, we investigated the feasibility of using TPOAC in the direct synthesis of hierarchical zeolite Y for use in FCC composite catalyst. We first optimized the synthesis of mesoporous Y zeolite at small (gram) scale. The most promising mesoporous zeolite was scaled up. For comparison, a bulk zeolite Y was prepared and its Al content was lowered by substitution of framework Al by Si. The acidic properties of the scaled-up zeolites, the composite catalysts derived thereof and the lab-deactivated and regenerated FCC catalysts were characterized in detail. The FCC performance of two lab-deactivated composite catalysts was evaluated in an Advanced Catalytic Evaluation (ACE) unit.

2. Experimental

2.1. Zeolite synthesis

For the synthesis of reference bulk zeolite Y, a seed gel was prepared by dissolving 4.04 g NaOH and 2.0 g $NaAlO_2$ in 19.97 g water. Then, 22.80 g sodium silicate solution (Prolabo, 25.5–26.5% SiO_2) was added dropwise under vigorous stirring. The resulting seed gel (gel A) was aged overnight at room temperature. In a second round bottom flask, a feedstock gel (gel B) was prepared. After dissolving 0.04 g NaOH and 3.31 g $NaAlO_2$ in 33.19 g water, 35.56 g sodium silicate (26 wt.% in water, Prolabo) was added dropwise under vigorous stirring. The Si/Al ratio of the feedstock gel was varied between 2.5 and 5.0 by adjusting the amount of sodium aluminate. To prepare the final synthesis gel, an amount of 4.46 g of the aged seed gel A was added to the feedstock gel B under vigorous stirring and was stirred for another hour. The resulting gel was transferred into a 125 mL Teflon-lined stainless-steel autoclave and heated in a static oven at 373 K for 24 h.

The gel for obtaining mesoporous zeolite Y was prepared in the same way as described above. Prior to the hydrothermal step, dimethyloctadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC, ABCR, 60 wt.% in methanol) was added dropwise to the synthesis gel; this gel was further stirred for 4 h. The Si/TPOAC ratio was varied between 10 and 125. The gels were then hydrothermally treated at 373 K for 72 h. The solid materials were recovered by filtration of the suspension, followed by washing with copious amounts of water. To remove TPOAC, the solids were calcined in artificial air (20/80 (v%/v%) O_2/He). The materials are denoted by FAU(x, y) with x being the SiO_2/TPOAC ratio (∞, 125, 45, 20, 10) and y the Si/Al ratio (2.5, 3.5, 5.0) in the starting gel.

A portion of the mesoporous zeolite Y prepared with an SiO_2/TPOAC ratio of 45 and an initial Si/Al ratio of 5.0 in the synthesis gel (Y(45,5.0)) was treated with ammonium hexafluorosilicate (AHFS). The zeolite was first ion-exchanged four times with 1 M KNO_3, followed by four exchange cycles with 1 M NH_4NO_3 under reflux. After drying the zeolite overnight, 10 g of zeolite was slurried in 100 ml of 3.4 M ammonium acetate at 348 K. An amount of 135 ml of 0.1622 M AHFS was added dropwise over a period of 2 h. The final slurry was stirred overnight at 348 K. The solid was recovered by filtration and washed with 1 L of hot (363 K) demineralized water. The washed solid was dried in a vacuum oven at 293 K.

The synthesis of several zeolite materials was scaled up by increasing the reactant amount by a factor of 16. The hydrothermal synthesis was done in an 1.5 L Teflon-lined autoclave. At this scale, a standard zeolite Y was synthesized at a Si/Al ratio of 2.5 and a mesoporous zeolite Y at a Si/Al ratio of 5.0 in the presence of TPOAC (SiO_2/TPOAC = 45). The Si/Al ratio of the microporous zeolite Y was increased by AHFS treatment according to the procedure outline above. The proton forms of these materials were obtained by suspending 1 g of calcined zeolite in 10 ml 1 M NH_4NO_3 for 4 h at 353 K. The ion-exchange was repeated twice. The final step was calcination in artificial air at 723 K for 4 h. The calcined zeolites are denoted as FAU(∞, 4.1)-large and FAU(45, 2.9)-large, reflecting the final Si/Al ratios as determined by ICP analysis.

Composite catalysts were prepared by spray-drying the zeolite with kaolin as filler and alumina sol as the binder. The resulting catalyst composite consisting of 35 wt.% zeolite, 50 wt.% kaolin and 15 wt.% alumina was subjected to steam-calcination to simulate catalyst regeneration. The composite catalysts were steamed at 1023 K for 4 h using 100% steam followed by calcination at 873 K for 1 h. The deactivated catalyst was then sieved to obtain particles in the range 38–212 μm and calcined at 873 K for 2 h.

2.2. Characterization

Elemental analysis was done by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Spectro CIROS CCD spectrometer equipped with a free-running 27.12 MHz generator at 1400 W. Zeolite samples were dissolved in a mixture of $HF/HNO_3/H_2O$ (1:1:1).

XRD patterns were recorded on a Bruker D4 Endeavor powder diffraction system using Cu Kα radiation with a scanning speed $0.01^\circ \cdot \min^{-1}$ in the 2θ range 5–60°. The crystallinity was determined according the standardized procedure ASTM D 3906–80. To this end, the intensities of the 15.7°, 18.8°, 20.5°, 23.8°, 27.2° and 34.3° 2θ reflections (corresponding to the [331], [511], [440], [533], [642] and [555] hkl planes) were taken after background subtraction and related to the intensities of the highly crystalline sample FAU(∞, 2.5) prepared in this work FAU(∞, 2.5).

Ar physisorption isotherms were measured at 87 K on a Micromeritics ASAP2020 system in static measurement mode. The samples were outgassed at 623 K for 8 h prior to the sorption measurements. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (S_{BET}) in the pressure range $p/p_0 =$ 0.05–0.25. The mesopore volume (V_{meso}) and mesopore size distribution were calculated using the Barrett–Joyner–Halenda (BJH) method on the adsorption branch of the isotherm. The micropore area (S_{micro}) and micropore volume (V_{micro}) were calculated from the t-plot curve using the thickness range between 3.5 and 5.4 Å [42].

Nuclear Magnetic Resonance (NMR) measurements were performed on a 11.7 Tesla Bruker DMX500 NMR spectrometer operating at 500 MHz for ^1H, 99 MHz for ^{29}Si and 132 MHz for ^{27}Al. The ^{27}Al MAS NMR was done using a Bruker 2.5-mm MAS probehead spinning at 20 kHz; ^{27}Al NMR spectra were recorded with a single pulse sequence with an 18° pulse duration of 1 μs and a interscan delay of 1 s. A saturated $Al(NO_3)_3$ solution was used for ^{27}Al NMR shift calibration. The ^1H and ^{29}Si MAS NMR measurements were carried out using a 4-mm MAS probehead with sample rotation rates of 12.5 kHz for ^1H and 10 KHz for ^{29}Si NMR measurements. ^1H and ^{29}Si NMR shifts were referred to Tetramethylsilane (TMS). Quantitative ^{29}Si NMR spectra were recorded using a high power proton decoupling direct excitation (HP-DEC) pulse sequence with a 45° pulse duration of 2.5 μs and an interscan delay of 160 s. For ^1H MAS NMR measurements, the zeolites were first dehydrated at a temperature of 723 K at a pressure lower than