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Co-catalytic cracking of n-decane and 2-ethylphenol over a variety of deactivated zeolites for the conversion of fossil- and bio-based feeds in Co-FCC

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ABSTRACT

The hydrothermal stability of a broad variety of large- and medium-pore zeolites was studied at 816 °C under steam atmosphere, in order to test their suitability as a catalyst material in the fluid catalytic cracking (FCC) process. The stability was evaluated by N_2 physisorption prior to and after the treatment. Several zeolites showed stabilities superior to the reference zeolite USY, which is commonly used as an FCC catalyst. The selection of hydrothermally stable zeolites was further subjected to catalytic cracking. As model components for fossil- and bio-based feeds, a mixture of n-decane and 2-ethylphenol (mass fraction 90 and 10%) was used in a fixed-bed reactor at 480 °C to investigate the potential of the catalysts in Co-FCC. Especially large-pore zeolites showed superior conversion and less profound deactivation over time on stream for co-feeding experiments. Though medium-pore zeolites and Beta gave high degrees of conversion for pure n-decane cracking, these zeolites deactivated very fast during co-cracking experiments. Furthermore, the use of FAU and EMT zeolites resulted in a deeper deoxygenation of the phenol molecule with higher selectivities to aromatics and water. This is believed to be due to the enhanced H-transfer reaction with those materials and shows why the faujasite material might still be the catalyst of choice, not only for FCC in general, but also for Co-FCC applications.

1. Introduction

The European Union (EU) has set itself the 20-20-20 targets [1]. In the year 2020, greenhouse gas emissions are supposed to be reduced by 20% compared to 1990, with an improvement in energy efficiency of also 20%. Furthermore, the proportion of renewables in the energy sector is aimed to be 20%, while in the transport sector a 10% share of renewables is pursued. In order to reach these and the long-term 2050 goals [2], an energy shift towards biomass is strongly needed.

The utilization of biomass to solve the addressed challenges is widely described in literature [3–6]. Due to ethical reasons, first-generation bio-fuels are no longer considered an option to satisfy the worldwide hunger for carbon-based energy as they are competing with food production [7]. Abundant residues from forests and agriculture are ideal raw materials and were depicted to be a reasonable substitute for the production of bio-based fuels [8]. The idea to co-feed biomass-derived oils in existing refineries received more attention over the last years, since this would need only low additional investment and operational costs. Fluid Catalytic Cracking (FCC) may be the best-suited process in an oil refinery because of its flexibility to adapt to changing feedstocks and product demands [9].

Lignin-based biomass can be converted via pyrolysis into a bio-oil. The pyrolysis oil consists of a heterogeneous mix of organic compounds, mostly oxygenated molecules e.g. acids, aldehydes, ketones, alcohols, esters, ethers, glycols and phenols [10–12]. Due to the variety of oxygenated functional groups, the pyrolysis oil cannot be stored for longer times, since it is not stable and requires upgrading to lower the oxygen content and to enable a better miscibility with the vacuum gas oil (VGO) in order to be co-fed into an FCC unit. Upgrading can be performed with molecular hydrogen

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via hydrodeoxygenation (HDO) over metal-containing solid catalysts. The reactivity of the oxygenated molecules in HDO was summarized by Mortensen et al. and Furimsky as follows [13,14]:

alcohol > ketone > alkylether > carboxylic acid ≈ m-/p-alkylphenol ≈ naphthol > phenol > diarylether ≈ o-alkylphenol ≈ alkylfuran > benzofuran > dibenzofuran.

The high activation energy for the conversion of the phenolic molecules explains the large amount of phenols found in an HDO oil [12,15] and describes the importance of this class of molecules as feed for Co-FCC.

Co-Processing of a bio-oil and a fossil-based VGO has already been successfully demonstrated by Petrobras (Brazil) in an FCC pilot plant [16]. Other authors reported on co-cracking experiments in a microactivity (MAT) set-up on a bench scale [7,17–21]. The main problem in Co-FCC is severe catalyst deactivation due to additional coke deposition originating from lignin and phenolic compounds in the bio-oil [7,18,19,21]. Higher amounts of coke may also lead to higher temperatures in the regenerator of an FCC unit and, therefore, to an irreversible destruction of the catalyst particle itself or the zeolitic component inside an FCC catalyst [21]. Most of these studies were performed with standard zeolites such as zeolite Y and ZSM-5 that are used in an FCC catalyst particle [22–24]. Some also describe the use of fresh [7,18,21] or equilibrated (E-CAT) FCC catalysts in co-cracking experiments [19]. However, the investigation of other zeolite materials for the application as a Co-FCC catalyst is mostly left aside in literature.

Studies about co-cracking of model paraffins with phenols as oxygenated compounds for a bio-oil on zeolites have been conducted as well by several authors [25–31]. The use of model compounds as substrates allows for a deeper understanding of the interaction of fossil- and bio-based molecules on the zeolite surface. Gueudré et al. reported on a synergy existing between the fossil- and bio-based feeds in which the addition of bio-components not only favors coking by itself but also increases the coking effect originating from the fossil feed confirmed by ^{14}C measurements of the coked catalyst [21]. Bulky alkylated phenolic species (lignin fragments) can be converted via hydride transfer from lighter alkanes, derived from cracking of fossil oil, into phenol or smaller substituted phenols [21]. The importance of the H-transfer reaction was also outlined by Resasco and coworkers to maintain catalyst stability in the conversion of anisole and m-cresol [30–32]. Furthermore, Wang and Rinaldi reported on the dehydroxylation of phenol in the absence of molecular hydrogen via hydride transfer reaction with isopropanol [33].

In this paper, we report on a study about the hydrothermal stability of a broad variety of different zeolites. This aspect is of utmost importance for FCC applications, because the catalyst particle is subjected to harsh conditions such as high temperatures and steam atmosphere in the regenerator of an FCC unit. Therefore, potential FCC zeolite candidates should be selected according to their hydrothermal stability. It is the goal of this study to cover a broad range of zeolites with different properties, such as framework type and/or modification. Faujasites as typical cracking catalysts were selected as well as completely different framework types. These also include MFI structures such as ZSM-5 with and without phosphorus, since phosphorus is known to stabilize the MFI structure [24]. Additionally, [Fe]ZSM-5 was added as it is also subject to investigations in reactions like selective catalytic reduction, where harsh hydrothermal conditions can be found [34,35]. In the second part of this study, we address the catalytic cracking of n-decane purely and in a mixture with 2-ethylphenol as a model component for a biomass-derived feed, over a series of hydrothermally deactivated zeolites.

2. Experimental

2.1. Origin and pretreatment of studied zeolites

Zeolites MCM-22 and Beta were supplied by SINTEF (Norway) and Clariant (Germany), respectively. Zeolites Y, USY, RE-USY and [Fe]ZSM-5 were supplied by GRACE (Germany). Amorphous silica-alumina was obtained from Akzo (Germany). All other zeolites were synthesized in house in earlier works. Zeolites in their sodium form were subjected to three aqueous ion exchange procedures with ammonium nitrate (1 M) at 80 °C to generate a sodium-free form.

2.2. Hydrothermal deactivation

In order to evaluate the hydrothermal stability, zeolites were pressed and sieved into particles of 200–315 μm size. About 7 mL bulk volume were placed in a fixed-bed reactor made of quartz glass and were heated to 816 °C under nitrogen with a flow rate of 60 mL/min. Once the temperature was stable, 30 mL of water were added over 5 h with a syringe pump. The hydrothermally deactivated zeolite was cooled down to room temperature under nitrogen afterwards. The hydrothermal deactivation procedure was on the basis of the AM-1500 method applied in industry [36,37]. For catalytic investigations, the fresh zeolites claimed as stable were only deactivated at 700 °C in steam atmosphere as described above in order to maintain a certain degree of activity.

2.3. Characterization

The stability of the zeolites was evaluated by means of N_2 physisorption. Isotherms were recorded at −196.15 °C prior and after hydrothermal deactivation on an Autosorb 3-B by Quantachrome. The t-plot method was used to distinguish between micropore and external surface area. The amount of coke deposited on the catalysts was determined by thermogravimetric measurements on a Setsys 16/18 by Setaram. The mass of coke calculated refers to the dry mass of catalyst. Chemical composition (sodium content and the n_{Si}/n_{Al} ratio) of the samples was measured by ICP-OES with a Vista-MPX CCD Simultaneous by Varian.

2.4. Catalytic cracking of n-decane and 2-ethylphenol

Catalytic studies with n-decane and 2-ethylphenol as substrates were conducted at 480 °C in a continuous flow fixed-bed reactor made of quartz glass. The dry mass of the hydrothermally deactivated catalyst was 600 mg, and the total mass flow of the substrate(s) 50 mg h^{-1}, resulting in a *weight hourly space velocity* of 0.08 h^{-1}. The catalyst particle size was 200–315 μm from prior hydrothermal treatment. Pure n-decane ($\geq$ 99%; Sigma-Aldrich) was enriched in nitrogen as carrier gas in a one-component saturator, whereas a mixture of n-decane and 2-ethylphenol (99%; Sigma-Aldrich) (mass fraction 90 and 10%) was enriched by means of a two-component saturator as described by Weitkamp and Dauns [38,39]. Substrates were used without further purification. Products were analyzed by an on-line gas chromatograph equipped with a PoraPlotQ column, hydrogen as carrier gas and a TCD and FID detector. A second GC with helium as carrier gas, a ShinCarbon column and a TCD and FID installed behind a cooling trap was used to identify CO and CO_2, although only traces were found. Conversion X of the substrates n-decane (n-Dec) or of the mixture n-decane and 2-ethylphenol (2-Et-PhOH) and selectivities/share in the product mixture S to a product j found at the reactor outlet were defined as in Equations (1) and (2). Since the carbon balance was closed to >95% and for the sake of convenience, the term selectivity