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Interplay between nanoscale reactivity and bulk performance of H-ZSM-5 catalysts during the methanol-to-hydrocarbons reaction

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ABSTRACT

H-ZSM-5 catalyst powders before and after a steaming post-treatment have been investigated during the Methanol-To-Hydrocarbons (MTH) process at 350 °C. Bulk and surface characterization techniques have been combined with in situ Scanning Transmission X-ray Microscopy (STXM) at the aluminum and carbon K-edge to study the changes in acidity, porosity, reactivity, and aluminum distribution upon steaming. It was found that steaming post-treatment has a positive impact on the stability of H-ZSM-5 without inducing important changes in the MTH activity and selectivity. The lower MTH stability of non-steamed H-ZSM-5 catalyst powder is related to the formation of poly-aromatic compounds in the outer regions of the catalyst particles, as probed with in situ STXM. In contrast, a limited amount of poly-aromatics was found in the outer rim of steamed H-ZSM-5 catalyst particles. These differences occur as a result of the generation of mesoporosity as well as the reduction in the number and strength of acid sites after steaming, as evidenced by the nanoscale imaging of adsorbed pyridine with STXM.

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1. Introduction

The Methanol-To-Hydrocarbons (MTH) process has attracted both industrial and academic interest as methanol can be produced at a large scale from syngas by the direct oxidative conversion of methane or by the reductive conversion of atmospheric carbon dioxide with hydrogen [1]. Depending on the reaction conditions and the type of catalyst used in the MTH process, methanol can be transformed into olefins (MTO), gasoline (MTG), or other value-added chemicals [2,3]. Since the first oil crisis, zeolite materials have been extensively studied as promising catalysts for the MTH process [4,5]. Among them, H-ZSM-5 is considered as one of the archetypal catalyst to conduct the MTH reaction [4]. Nonetheless, the generation of undesired carbon deposits often leads to severe diffusion restrictions and fast deactivation rates. As a result, H-ZSM-5 needs to be regenerated, which frequently induces leaching of framework Al species, resulting in important variations in activity, selectivity as well as overall stability [6,7].

In the present work, the effect that a mild hydrothermal treatment has on the MTH stability of relevant zeolite H-ZSM-5 catalyst powders has been investigated in detail. We compare the reactivity of a calcined (sample name: H-ZSM-5-C) and a mildly steamed (sample name: H-ZSM-5-500) catalyst powder during the MTH reaction at 350 °C by catalytic testing and in situ Scanning Transmission X-ray Microscopy (STXM) at the carbon and aluminum K-edges as well as by a range of bulk and surface characterization methods. This unique experimental approach allows proposing an explanation of the large differences noticed in MTH stability between H-ZSM-5-C and H-ZSM-5-500 in terms of nanoscale differences in the type and amount of hydrocarbon deposits in addition to the number and strength of acid sites within individual zeolite H-ZSM-5 aggregates.

2. Experimental

2.1. Materials

Two different zeolite H-ZSM-5 aggregate materials, namely a calcined material (i.e., H-ZSM-5-C) and a mildly steamed material (i.e., H-ZSM-5-500), have been investigated. The starting material, with crystallite dimensions of approximately 200–800 nm, is a commercial zeolite NH_4-ZSM-5 catalyst powder provided by Zeolyst (CBV2314, Si/Al = 11.5). To obtain H-ZSM-5-C, the starting

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material was calcined in a static oven (N100 Nabertherm) first preheating it at 120 °C (30 min, 2 °C/min) and then increasing the temperature to 550 °C (360 min, 10 °C/min). The steamed sample was prepared treating H-ZSM-5-C in a quartz tubular oven (Thermoline 79300) during 180 min at 500 °C via saturation of a nitrogen flow (180 ml/min) with water at 100 °C. Prior to steaming, the sample was preheated at 120 °C (30 min, 2 °C/min). After the hydrothermal treatment, the sample was calcined following the same procedure as that described to obtain H-ZSM-5-C.

2.2. X-ray diffraction

X-ray diffraction (XRD) patterns were obtained at room temperature from 5° to 90° 2θ with a Bruker-AXS D8 Advance powder X-ray diffractometer, equipped with an automatic divergence slit, a Våntec-1 detector and a Cobalt Kα 1,2 (λ – 1.79026 Å) source.

2.3. Nitrogen physisorption

Nitrogen adsorption and desorption isotherms were measured at −196 °C on a Micromeritics Tristar 3000 instrument.

2.4. Catalytic testing

Catalytic testing experiments were performed on the powders without pressing and sieving the two catalyst materials under study. For each experiment, 30 mg of catalyst was placed in a fixed-bed reactor, activated at 550 °C under oxygen for 1 h, and then cooled to the reaction temperature (350 °C). The MTH reaction products were analyzed with an online gas chromatograph (GC) connected to the outlet of a fixed-bed reactor (i.d. 6 mm) using a heated transfer line. The inlet of the reactor was connected to helium, which was bubbled through methanol kept at 20 °C (P_{MeOH} = 130 mbar) in a saturation evaporator (WHSV = 5.56 g g^{-1} h^{-1}).

To analyze the coke after reaction, 15 mg of the deactivated catalyst samples was transferred into a Teflon tube where 1 ml of 15% hydrofluoric acid was added. Subsequent to a waiting time of 30 min, 1 ml of dichloromethane, containing hexachloroethane as the internal standard, was added to the Teflon tube. Then, 1 μl of the resulting organic phase was analyzed in an Agilent 6890N GC equipped with an Agilent 5793 Mass Selective Detector. A HP-5MS column (60 m, 0.25 mm i.d., stationary phase thickness 0.25 μm) and an inlet split of 1:5 were used for this purpose.

2.5. Scanning transmission X-ray microscopy

In a first set of in situ STXM experiments, the MTH reaction was performed on the interferometrically controlled STXM microscope at the Pollux beamline of the Swiss Light Source (SLS, Villigen, Switzerland) [8]. For this purpose, a Micro-Electro-Mechanical System (MEMS) nanoreactor was used to characterize the catalytic behavior of the two zeolite H-ZSM-5 catalyst powders under study. Prior to reaction, the samples were introduced inside the nanoreactor and placed in an adaptor that can be translated with nanometer precision by an interferometrically controlled (x,y,z) piezoelectric stage. The samples were activated at 450 °C flowing helium (2 ml/min) during 30 min. Then, the temperature was decreased to 350 °C, and methanol (Antonides-Interchema, 99%) was introduced via saturation of helium flow (2 ml/min) at 0 °C for 400 min. During reaction, the absorption at the carbon K-edge was analyzed at different times on stream collecting a series of images over small energy increments, subsequently combining these images to form a spectral image sequence (stack). The stacks were obtained in the range of 280–310 eV using an energy resolution of 0.2 eV. In a second step, a Principal Component Analysis (PCA) and a cluster analysis were performed to classify pixels according to statistical similarities in their spectra. During the measurements, the monochromized X-ray beam was focused to a spot size of 35 × 35 nm using a Fresnel Zone plate. The pixel size used in the carbon K-edge STXM image sets was 35 nm.

In a second set of STXM experiments, ex-situ aluminum K-edge measurements were done at beamline 10.ID.1 of the Canadian Light Source (CLS, Saskatoon, Canada) using a 35 nm zone plate. In every case, the samples were placed on silicon nitride windows (100 nm thickness) and mounted perpendicular to the beam on a piezoelectric stage. The aluminum stacks were recorded in the 1555–1590 eV range with an energy resolution of 0.15 eV and a spatial resolution of 70 nm. Aluminum reference compounds were measured performing a line scan along the samples with a dwell time of 4 ms and an energy resolution of 0.15 eV. Normalization and background correction was done subtracting to every spectrum a second spectrum obtained from an aluminum-free region. The aluminum K-edge X-ray absorption spectra (XAS) of these reference compounds were used to perform a least squares linear combination fitting of the aluminum stacks obtained from both H-ZSM-5-C and H-ZSM-5-500. The STXM data files were analyzed using aXis2000 software.

In a third set of STXM experiments, pyridine adsorption experiments were performed on the interferometrically controlled microscope at beamline 11.0.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL, Berkeley, USA) [9]. Prior to pyridine adsorption, 20 mg of zeolite sample was heated (170 °C) in a round-bottom flask under vacuum (10^{-3} - mbar) for 60 min. Subsequently, the samples were prepared adding 0.2 μl of pyridine (Acros Organics, 99%). After a waiting time of 60 min, pyridine was partially removed by heating the samples at 400 °C for a period of 60 min. During the STXM experiments, the samples were placed on silicon nitride windows (100 nm thickness) and mounted perpendicular to the beam on a piezoelectric stage. The monochromatized X-ray beam was focused to a spot size of 25 × 25 nm using a Fresnel zone plate. The absorption at the carbon K-edge was measured in the range of 280–310 eV collecting a series of stacks with an energy resolution of 0.2 eV. After spatially aligning the stack, PCA was used to obtain the primary components in the data set. Subsequently, a cluster analysis was performed to classify pixels according to statistical similarities in their spectra. The pixel size used in the image sets was 30 nm.

2.6. Temperature-Programmed Desorption

Temperature-Programmed Desorption (TPD) measurements with ammonia as probe molecule were performed using a Micromeritics AutoChemII 2920 apparatus. The sample, 0.15 g in both cases, was first pretreated in helium (25 ml/min) for 30 min at 600 °C, then cooled down to 100 °C, and saturated with ammonia to its equilibrium state. Prior to desorption, samples were flushed in helium for 30 min. Subsequently, ammonia desorption was performed in the range of 100–600 °C at a heating rate of 10 °C/min.

2.7. Sputter depth profiling X-ray Photoelectron Spectroscopy

Sputter depth profiling X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a Physical Electronics Quantum 2000 Scanning X-ray Photoelectron Spectrometer or a Physical Electronics Quantera X-ray photoelectron spectrometer. In either instrument, the base pressure was kept $\sim 1 \times 10^{-9}$ mbar. The XPS spectra were collected using monochromatic aluminum Kα radiation (1486.6 eV). Charging was neutralized using the combined low energy electron flood gun and low energy argon ion gun of the instrument. Survey scans were collected using a pass energy of 187 eV and region scans with a pass energy of 58 eV. For typical measurements, H-ZSM-5 zeolites were deposited onto a vitreous

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