



Single-catalyst particle spectroscopy of alcohol-to-olefins conversions: Comparison between SAPO-34 and SSZ-13



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ABSTRACT

The formation of distinct hydrocarbon pool (HCP) species on individual micron-sized SAPO-34 and SSZ-13 crystals have been compared during methanol-to-olefins (MTO) and ethanol-to-olefins (ETO) conversion processes. In situ UV–vis micro-spectroscopy reveals the formation of 400 nm and 580 nm absorption bands, which are ascribed to poly-alkylated benzene (PAB) carbocations, the most active HCP species and poly aromatics (PA) the deactivating species, respectively. PAB formation within both catalysts is fitted with first-order kinetics at low reaction temperatures and activation energies (E_a) can be calculated, while PA/PAB ratio is calculated to monitor the deactivation process for different reaction temperatures. The results show that for both activation and deactivation processes, methylation reactions are leading in MTO and are controlled by acid strength; while olefins condensation reactions are governing in ETO and are affected more by acid site density. Moreover, the distribution of HCP species is visualized by confocal fluorescence microscopy, which demonstrates that the acid site density plays an important role on the local catalytic performance. Finally, synchrotron-based IR micro-spectroscopy reveals different activity of the two catalysts as shown by the intensity and frequency of distinct characteristic bands.

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1. Introduction

Light olefins, such as ethylene and propylene, have been widely used as raw materials for the production of e.g. polymers [1,2]. However, the current high price of crude oil as well as more stringent environmental legislation have spurred great interests in developing new and improved catalytic technologies based on alternative feedstocks, such as methane and biomass. Among these processes, the conversion of alcohols (e.g. methanol and ethanol) to light olefins have received strong research attention [3,4]. Methanol can be produced from synthesis gas ($\text{CO} + \text{H}_2$), which can be obtained from almost any gasifiable carbon source, such as natural gas, coal, biomass and agricultural waste [5]. The methanol-to-olefins (MTO) process was discovered in 1976 and significantly improved by the discovery of the SAPO-34 material by Union Carbide [1,6]. Furthermore, the ethanol-to-olefins (ETO) process has received recent attention owing to the interest in the

full utilization in the production and use of bio-ethanol, which can be obtained in large quantities from modern lignocellulosic biorefineries [1,7].

MTO and ETO processes can be efficiently catalyzed by various protonated zeolites or zeotype materials, among which SAPO-34 with large cavities ($6.7 \text{ \AA} \times 10.9 \text{ \AA}$) interconnected through small windows ($3.8 \text{ \AA} \times 3.8 \text{ \AA}$) is currently one of the archetypal industrial MTO catalysts, giving up to 80% total carbon yield of propylene and ethylene [8]. Moreover, the CHA topology is one of the few where both the silicoaluminophosphate (SAPO-34) and aluminosilicate (SSZ-13) analogs are readily synthesized [9]. It has been reported that SSZ-13 displays higher acid strength than SAPO-34 [10]. As a consequence, an enhanced production rate of olefins as well as aromatics retained in the catalyst pores was observed for SSZ-13, leading to a lower optimal temperature of operation [9].

Understanding the reaction mechanism and related deactivation pathways during catalytic processes are important topics as this knowledge can be further translated into designing new and improved catalyst materials. In the case of MTO, there is a general consensus that the reaction follows the hydrocarbon pool (HCP) mechanism, in which methanol is subsequently added to an organic scaffold [11–14]. While when using ethanol as a feed over H-ZSM-5, an almost identical product distribution is found as for the MTO

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process. This suggests that ETO likely proceeds through similar HCP pathways [15]. Further investigations have shown that the trapped species within the zeolite channels after ETO are very similar than those found after MTO, although they contain a higher amount of ethyl-substituted molecules [16,17]. The formation of hydrocarbon species and their activity critically rely on the combination of reaction conditions, size of the cages/channels of the molecular sieves as well as the acid site density and strength [5,14,18,19]. However, active HCP species are often alkylated benzene molecules and their protonic counterparts [1,2,18,20]. Furthermore, these active species in SAPO-34 readily convert into larger aromatics that eventually block the active sites and hinder the diffusion of reactants as well as products [22,23]. Thus, the coke formation can affect the catalyst performance as it provokes variations in activity and selectivity. In the past decades, there have been intensive studies investigating the nature of the coke species and their formation mechanism by using a variety of analytical tools, such as IR, UV-vis, electron spin resonance (ESR), nuclear magnetic resonance (NMR), gravimetric (TEOM & TGA) and X-ray photoelectron spectroscopy (XPS) [24–27]. Nevertheless, the number of methods that allows the investigation of the coke formation under realistic reaction conditions is limited and even further diminishes when non-invasive methods or spatial resolution criteria are requested, which is crucial considering the dynamic nature of the catalyst system.

Recently, our group has reported that in the case of SAPO-34, the active aromatic species, alkylated benzene carbocations, follow different formation pathways during MTO and ETO by using a set of micro-spectroscopy techniques [21]. In this work, we extend this mechanistic approach for the study of individual SSZ-13 crystals, an aluminosilicate with CHA structure, stronger acid sites and in this specific case lower acid site density. We also include here an investigation of the formation of bulkier poly aromatic species, which are believed to deactivate the material. These results will be compared with SAPO-34 ones and after that, the role of acid strength and acid site density on the kinetics, location and nature of distinct hydrocarbon species during activation and deactivation in MTO and ETO processes will be assessed.

2. Experimental

2.1. Materials and experiments

The as-synthesized SAPO-34 and SSZ-13 materials under study have crystal sizes of $50 \times 50 \times 50 \mu\text{m}^3$ and $40 \times 40 \times 40 \mu\text{m}^3$, respectively. Their synthesis procedure has been reported elsewhere [28,29]. The Si/(Al+P) and Si/Al ratios are 0.204 and 17.7, which can be translated theoretically into two acid sites per cage for SAPO-34 crystals and two acid sites per three cages for SSZ-13 crystals. The crystals were placed on the heating stage of an in situ cell (Linkam FTIR 600) equipped with a temperature controller (Linkam TMS 93) where they were heated. During each measurement, the calcined crystals were first heated to 673 K at a rate of 15 K min^{-1} , then heated to 823 K with a rate of 5 K min^{-1} , and held at this temperature for 1 h under N_2 atmosphere. Subsequently, the temperature was brought to the required reaction temperature at a rate of 15 K min^{-1} after which the N_2 was flowing through methanol or ethanol thereby acting as carrier gas.

2.2. N_2 physisorption analysis

N_2 -physisorption isotherms were recorded using a Micromeritics Tristar 3000 set-up operating at 77 K. Prior to physisorption measurements, all samples were degassed for 12 h at 573 K in a nitrogen flow. BET surface areas were determined using 10 points

between 0.06 and 0.25. Micropore volumes ($\text{cm}^3 \text{ g}^{-1}$) were determined by *t*-plot analysis for *t* between 3.3 and 5.4 \AA to ensure inclusion of all five minimum required pressure point.

2.3. Ammonia temperature programmed desorption

Acidity was investigated by temperature-programmed desorption (TPD) of ammonia under He flow (25 ml min^{-1}) using a Micromeritics Autochem II equipped with a TCD detector. 50 mg of catalyst was loaded and dried at 873 K for 1 h, then cooled down to 373 K. After that, pulses of ammonia were introduced up to saturation of the catalyst material. The TPD was performed up to 873 K with a heating ramp of 5 K min^{-1} .

2.4. In situ UV-vis micro-spectroscopy

The UV-vis micro-spectroscopy measurements were performed with an Olympus BX41 upright microscope using a $50 \times 0.5 \text{ NA}$ high working-distance microscope objective lens. A 75 W tungsten lamp was used for illumination. In addition, the microscope has a 50/50 double viewpoint tube, which accommodates a CCD video camera (ColorView Illu, Soft Imaging System GmbH) and an optical fiber mount. A $200 \mu\text{m}$ core fiber connects the microscope to a CCD UV-vis spectrometer (AvaSpec-2048TEC, Avantes BV).

2.5. In situ confocal fluorescence microscopy

The confocal fluorescence microscopy studies were performed with a Nikon Eclipse LV150 upright microscope with a $50 \times 0.55 \text{ NA}$ dry objective lens. The confocal fluorescence microscopy images were collected with the use of a Nikon-Eclipse C1 head connected to the laser light sources (488 and 561 nm). The emission was detected with two photomultiplier tubes in the range 510–550 and 575–635 nm for the two lasers, respectively (in order to avoid channel overlap).

2.6. In situ synchrotron-based IR micro-spectroscopy

Synchrotron-based IR spectra were collected at beamline SMIS located at the French National Synchrotron SOLEIL (Paris, France). A Thermo Nicolet NEXUS 70 spectrometer, coupled to a Continuum XL microscope was used with the synchrotron light as the IR source. The microscope was equipped with a $15 \times 0.5 \text{ NA}$ Schwarzschild objective, a motorized *x* and *y* mapping stage and an adjustable rectangular aperture. For typical MTO and ETO measurements, the SAPO-34 crystals were placed in the in situ cell (Linkam FTIR 600) and heated up to 723 K in dry air (heating rate 15 K min^{-1}) for 30 min to activate the molecular sieves. Subsequently, the in situ cell was brought to reaction temperatures (15 K min^{-1}), and the alcohols were fed into the cell with several pulses. Spectra were collected during and after each pulse. For each measurement, the crystals were placed on a CaF_2 window located on the motorized (in *x/y*) mapping stage, recording the mid-IR ($4000\text{--}1300 \text{ cm}^{-1}$) spectrum in transmission mode with a spectral resolution of 4 cm^{-1} and 32 or 16 scans co-added. An aperture of IR beam $20 \times 20 \mu\text{m}^2$ was used to follow the MTO and ETO reactions in situ. Background measurements were performed with a spectral resolution of 4 cm^{-1} and 64 scans per spectrum.

3. Results and discussion

3.1. Textural properties and acidity of the materials

Table 1 summarizes the textural properties of the two materials under study, i.e., SAPO-34 and SSZ-13, as measured by N_2

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