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Growth mechanism of coke on HBEA zeolite during ethanol transformation

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ABSTRACT

HBEA (11) zeolite was deactivated rapidly by coking during the ethanol transformation into hydrocarbons, at 623 K and 30 bar. The nature of carbonaceous deposit was studied, after zeolite dissolution by hydrofluoric acid both by gas chromatography coupled with mass spectrometry and by matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). The coke on the external zeolite surface was characterized directly on the spent catalyst by laser desorption/ionization time of flight mass spectrometry (LDI-TOF MS). The coke species were identified and classified into 17 families following their unsaturation number (4–23). The coke was polyaromatic, and it was very alkylated (methyl, ethyl, and propyl groups). It is compounded of alkylbenzenes, mainly hexamethylbenzene (HMB), and alkyl-pyrenes, located within the zeolite pore, which could migrate to the external zeolite surface and grow into polyaromatic compounds constituted up to eight aromatic rings and up to 40 carbon atoms. Pulsed electron paramagnetic resonance spectroscopy measurements and molecular simulation by using Cerius^2 software have shown that HMBs are distant of 0.6 nm inside the zeolite pores.

1. Introduction

The catalytic conversion of ethanol to higher hydrocarbons than ethylene (C_{3+}) is a promising way to incorporate a high level of renewable carbon to gasoline pool. Ethanol to hydrocarbons (ETH) reaction can occur over different types of zeolites (BEA, MFI, FAU, etc.) [1]. But, ethanol transformation includes side reactions leading to the formation of carbonaceous materials, designated as "coke" [1–5]. The "coke" poisons active sites and/or blocks their access [6]. It is well demonstrated that these products are formed and trapped in the zeolite pores, and their formation can be considered as a "ship in the bottle" process [6]. In other words, the growth of these products depends on the shape and dimension of the zeolite pores. These coke molecules, trapped in the zeolite micropores being relatively simple, could act as active species in hydrocarbons transformation. Indeed, on medium pore zeolite, HZSM-5, the formation of C_{3+} hydrocarbons was observed even when the catalyst was saturated with coke molecules, mainly polyalkylbenzenes. Deep characterizations of coke showed the existence of radical species [2–5]. Madeira et al. assume that ethanol transformation into hydrocarbons occurs on radical coke molecules as active site [4,5]. But, in the case of wide pore zeolites (HFAU, HBEA), spatial constraints are different (diffusion inside the pores, channel size, proximity of molecule to wall) allowing recombination, condensation, cyclization reactions, etc. and consequently to polyaromatic compounds as result.

The chemical nature of coke components and precursors can be specified by spectroscopic characterization of coked zeolites with various techniques: infrared (IR), Raman [7], UV–visible [8], nuclear magnetic resonance (NMR) [9], and electron paramagnetic resonance (EPR) [2–5,10]. This last technique allows to characterize and quantify the nature of radicals generated during coke formation. But, the only way to determine the chemical composition of carbonaceous deposits, that is, the complete distribution of their components, is to remove "coke" from the zeolite by dissolving it in a solution of hydrofluoric acid [11]. A large part of coke components can be solubilized in organic solvents and analyzed by classical techniques such as GC, HPLC, NMR, IR, MS, and especially GC–MS. Unfortunately, the characterization of heavy molecules (>400 g mol^{-1}) is much more restricted. However, significant advances have been recently achieved with the use of (MA)LDI-TOF MS (matrix-assisted) and LDI-TOF MS (laser desorption/ionization time of flight mass spectroscopy) [12–14]. These techniques, which differ only by the adding (or not) a matrix (typically aromatic acid) to the sample, were recently applied in the characterization of heavy carbonaceous compounds, either directly on spent catalyst or on coke recovered from the catalyst. The primary advantage of the laser desorption/ionization is the relatively low energy input, which minimizes the fragmentation. Thus, the measured mass

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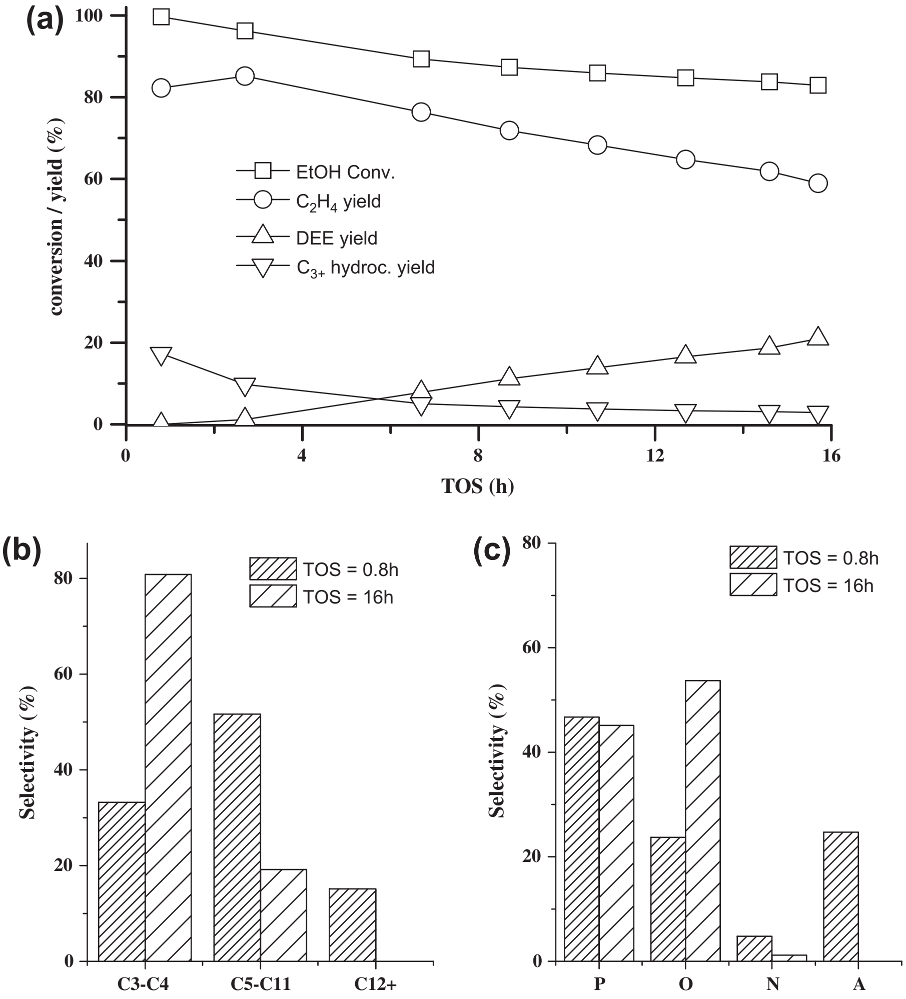

Fig. 1. Ethanol conversion over HBEA, at 623 K and 30 bar, DEE, ethylene and C_{3+} hydrocarbons yield (a); C_{3+} hydrocarbons distribution by number of carbon atoms (b) and chemical family (PONA) (c). "Data from [1]".

Table 1
Pore volumes and acidity for fresh and coked HBEA zeolite after the catalytic test (TOS = 16 h, T = 623 K, N_2/EtOH = 4, P = 30 bar). Data from [1].

	%C (wt.%)	Acidity[a] (μmol g^{-1})		Pore volume (cm^3 g^{-1})		
		Brønsted	Lewis	Total	Micro	Meso
Fresh		266	249	0.835	0.271	0.563
Coked	13.2	13(95%)	32 (87%)	0.150 (82%)	0.052 (81%)	0.098 (83%)

[a] Number of acid sites able to retain pyridine at 423 K (xx%) = loss.

spectrum directly represents the molecular weight distribution of the analyzed mixture.

This work seeks to deepen the coke composition and location formed over HBEA zeolite during ethanol transformation. For that, a variety of characterization techniques on the deactivated catalyst and on extracted coke is used.

2. Experimental

2.1. Ethanol transformation

HBEA (Si/Al molar ratio = 11) is a commercial material from Zeolyst International, UK. The sample was compacted, crushed, and sieved to obtain 0.2–0.4 mm homogeneous particles. Prior to catalytic testing, it was activated in situ under nitrogen flow (3.3 L h^{-1}) at 773 K and a total pressure of 30 bar. The catalytic test was carried out in a continuous down flow fixed bed reactor under a total pressure of 30 bar and at 623 K. The catalyst (0.3 g) was placed in the middle of the reactor (stainless steel, 40 cm long, 1.3 cm internal diameter, and 1.7 cm external diameter). Ethanol (96%, V/V) was fed into the reactor at 2 mL h^{-1}, corresponding to a N_2/EtOH molar ratio of 4 and a WHSV of 15 h^{-1}. Reaction products were analyzed by online gas chromatography using a VARIAN 3800 gas chromatograph equipped with two detectors: a FID detector (J&W PONA capillary column) and a TCD detector (5A sieve + Porabond Q).

2.2. Spent catalyst characterizations

The amount of carbon in the spent catalyst was measured using a CE instrument NA2100 PROTEIN elementary analyzer.