Mechanisms of coke growth on mordenite zeolite

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A B S T R A C T

Mechanisms of coke formation and growth transformation on MOR zeolite were investigated using a microbalance at 623 K for two propene pressures: 0.1 and 1 bar. The low and high coking pressures correspond to laboratory and industrial conditions, respectively. Initial coke deposition is faster at high pressure, but the maximum uptake is higher at low pressure. The complete determination of chemical composition of coke has required the use of a lot of techniques (IRFT, GC–MS, MALDI-TOF). From the change of chemical composition of coke, it can be proposed by different mechanisms of growth of coke molecules trapped in the zeolite micropores. The coke grows under industrial conditions (high olefins pressure) by successive alkylation/cyclization/aromatization reactions, while under laboratory conditions (low olefins pressure) the growth proceeds preferentially by condensation of coke molecules.

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1. Introduction

Many zeolite-catalyzed processes are prone to the deactivation by coking, leading to either a poisoning of the acid sites and/or a blockage to their access. The deactivation modes and the size and shape of the coke molecules are practically independent of the reactant; they depend mainly on the zeolite pore structure. Indeed, with monodimensional zeolite (e.g. MOR) deactivation occurs only through pore blockage [1], with tridimensional zeolites such as MFI [2] and FAU [3], the deactivation mode (with increase in coke content) passes successively from poisoning to pore blocking, and finally coke formation is, at high temperature, a shape-selective process [4]. A general scheme for coke formation and growth, proposed by Derouane [5] and then refined by Guisnet and Magnoux [6], is a succession of reactions starting from acyclic species and in which oligomers and cyclic species are considered as intermediate species and aromatics as coke precursors:

Alkanes → alkenes → oligomers → cycloparaffins
        → monoaromatics → polyaromatics → coke
        → heavy coke.

Even though it is a complex process, the number of elementary reaction families involved in the formation of coke precursors is limited, i.e. hydride transfer, alkylation, cyclization and deprotona-

tion [6]. The conversion of coke precursors to coke occurs either by a series of alkylation of the side chain or the nucleus of coke precursors [7], or by a dehydrogenating coupling of two adjacent coke molecules [8]. The proportion between these two growth mechanisms should depend on both the partial pressure of alkylating agent and coke content; the coke growth by alkylation is faster than its aging which occurs by condensation [1,9]; within zeolite micropores, light olefins diffuse more rapidly than polyaromatic compounds. Even that the growth of coke precursors is limited to the size and shape of the zeolite pores, a coke molecule rooted close to the external surface, in pore mouth, can continue to grow up to more than six aromatic-rings overflowing onto the outer surface of the zeolite crystal [10]. The deep characterization of these heavy coke molecules (molar weight > 300 g/mol) is restricted due to lack on solubility in most common solvents [11]. Significant advances have been achieved with the use of matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF/MS) [12–14]. Pinard et al. [15] proposed different mechanisms of coke growth, drawn from identification and distribution of heavy coke molecules by MALDI-TOF/MS: on BEA zeolite the coke grows by alkene alkylation [15] whereas on MFI zeolite was by condensation of coke molecules [16].

The aim of this study was to determine the impact of the pressure of alkylating agent (propene) on the mechanism of coke growth on a mordenite zeolite (MOR), known to promote heavy coke molecules [2]. A high pressure of propene is used in order to simulate the growth of coke during industrial conditions while the low pressure is typical of study in laboratory. The coking reac-

tion will be carried out by microgravimetry under high and low pressures of propene and the chemical composition of coke will be determined at different coking time. A special attention will focus on the chemical composition of the heavy coke.

2. Experimental

2.1. Material and characterizations

The zeolite used is a commercial mordenite supplied by Clariant in protonic form with a Si/Al molar ratio of 11. Its properties are already described in Ref. [17], and they are summarized in Table 1. Fresh and spent samples were characterized by transmission electronic microscopy (TEM) using a Philips CM 120 microscope equipped with a LaB$_6$ filament. Scanning Electron Microscopy/microscopy energy-dispersive X-ray (SEM/EDX) pictures were recorded on a Tescan (MIRA/LMH) microscope equipped with a field emission gun. SEM/EDX allows determining the length of the accessible micropores of zeolite crystals [18]. Textural properties were determined by sorption measurements of nitrogen at 77 K, by Micromeritics ASAP 2000 gas adsorption analyzer. Prior to measurement, samples were outgassed at 363 K for 1 h and 623 K for 4 h. Coked samples were outgassed at 363 K for 1 h and 423 K for 1 h to avoid coke elimination. The FT-IR measurements were carried out in a Nicolet 750 Magna FTIR 550 spectrometer (resolution 2 cm^{-1}). Samples were pressed into thin wafers and activated in situ in the IR cell under secondary vacuum (10^{-6} mbar) at 623 K and 423 K for the fresh and spent zeolites, respectively. The acidity of the samples was measured by infrared spectroscopy of adsorbed pyridine. The concentrations of Brønsted and Lewis acid sites were calculated from the integrated area, after pyridine adsorption at 423 K, of the protonated and coordinated pyridine bands at 1545 and 1450 cm^{-1}, respectively.

2.2. Microgravimetric experiments

The kinetics of coking were determined by microgravimetry using a sartorius 4433 microbalance at 623 K under static conditions by exposing 0.05 g of catalyst shaping in particles of 0.2–0.4 mm diameter to a constant pressure of propene (0.1 and 1 bar). Before introduction of cocking agent, zeolite was pretreated under primary vacuum (10^{-2} mbar) at 623 K for 10 h. Propene was introduced with the chosen pressure, and the decrease in propene pressure was negligible during zeolite coking.

2.3. Coke extraction

The coke located on external surface was extracted by washing spent catalyst with CH$_2$Cl$_2$ at 313 K under 100 bar nitrogen pressure during 10 min on a Dionex ASE 350 apparatus. In order to release molecules trapped in zeolite pores, the spent catalyst was dissolved in 51 vol% hydrofluoric acid solution at room tempera-

ture during 20 min. HF was neutralized by an acid boric solution and sodium hydrogen carbonate. The residue was extracted by CH$_2$Cl$_2$, but in certain cases, a fraction of coke remains insoluble in CH$_2$Cl$_2$ (black particles). This insoluble coke fraction was totally recovered, dried and weighted. The soluble coke fraction obtained after CH$_2$Cl$_2$ evaporation is analyzed and quantified by GC–MS (Thermoelectron DSQ) and GC–FID (Agilent), respectively. The low temperature of treatment by HF, the short contact time of the acid solution and the coke components as well as the very small contact area between mineral and organic phases allow to avoid any change of coke composition.

The soluble and insoluble coke fractions were characterized by MALDI-TOF MS on a Brüker Autoflex Speed mass spectrometer in a reflectron positive mode, where ions were generated by a 337 nm wavelength nitrogen laser. 10 mg of the extract (soluble or insoluble coke fractions) was suspended in 500 μL of THF and was mixed with dithranol as MALDI matrix (6 g/L in THF). After sonication, about 0.5 μL of this mixture was hand spotted onto the stainless steel target and dried at room temperature. Analyses were achieved using pulsed ion extraction (delay time 130 ns). The laser power was adjusted slightly above the threshold of desorption/ionization process and the spectra were the sum of 40,000 shots. The spectra presented in this paper were from raw data with baseline correction and no signal smoothing.

3. Results and discussions

3.1. Kinetics of coke formation

The formation of coke from propene on MOR zeolite was investigated in a microbalance at 623 K. Fig. 1 compares the time evolution of mass uptake of zeolite at 0.1 ($P_{0.1}$) and 1 (P_1) bar. There is a rapid initial deposition of coke followed by a slow increase. Although coke deposition is initially faster at P_1, it is higher at $P_{0.1}$ after 48 h (Fig. 1a). The deactivation by coking under industrial conditions is most probably faster (high pressure of olefins) than under laboratory ones. The rate of coke deposition (derivative of the coke uptake curve, Fig. 1b and c) initially 2.5 times higher at P_1 than $P_{0.1}$, decreases rapidly and approaches zero after only 1 h corresponding to ca 6–8 wt% of coke; note that the rates are not equal to zero but only very low. This step kinetically slow should probably correspond to growth of coke molecules formed during the short initial stage. Fig. 2 displays the changes of pore volume (V_p) and Brønsted acidity ([PyH$^+$]) of MOR zeolite as functions of time and coke amount. The losses of [PyH$^+$] and V_p are extremely fast regardless of the pressure of reactant; 2 wt% of coke is enough to suppress both 60% of V_p and 90% of acid sites (accessible to pyridine). This high toxicity of coke is common on MOR zeolite due to its monodimensional structure; one coke molecule in the entrance of the channel makes inaccessible all sites located in this channel [1,3].

Table 1
Main properties of the commercial mordenite zeolite.

Crystal[a] size (nm)	S_{BET}[b] (m^2 g^{-1})	S_{ex}[c] (m^2 g^{-1})	V_{micro}[c] (cm^3 g^{-1})	V_{meso}[d] (cm^3 g^{-1})	[PyrH$^+$][e] (μmol g^{-1})	[PyL][e]
100	524	23	0.20	0.06	1056	31

[a] Apparent size determined by TEM image (Fig. 3).
[b] Specific surface area measured by BET.
[c] External surface and micropore volume using *t*-plot method.
[d] Mesopore volume = $V_{total} - V_{micro}$ (V_{total}: determined from the adsorbed volume at $p/p_0 = 0.96$).
[e] Measured by pyridine adsorption on Brønsted (PyH$^+$) and Lewis (PyL).