



New routes for complete regeneration of coked zeolite



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ABSTRACT

Among alternative techniques to overcome the difficulties associated with thermal regeneration of coked zeolite, non-thermal plasma can be considered as one of the most promising technology. A complete regeneration of zeolite can be achieved at room temperature with a low energy consumption. The active species responsible for catalyst regeneration are the short-lived oxygenated species and not ozone. Based on EPR analysis, which allows the mapping of radicals, the active species generated by NTP are able to diffuse within zeolite eliminating coke molecules. The efficiency of regeneration is directly related to the number of active species present in gas phase. A simple way to increase their concentration consists to substitute N₂ by a noble gas as He. In this case, coke is totally oxidized into CO₂, 6 times faster than under air.

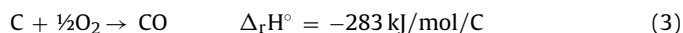
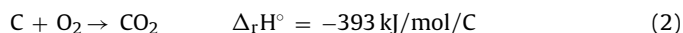
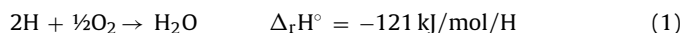
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1. Introduction

Catalyst deactivation, is a problem of great and continuing concern in industrial catalytic processes. The cost to industry for catalyst replacement and/or regeneration is estimated at several billions of dollars per year [1]. The question that determines the future of the deactivated catalyst, i.e. rejuvenation, regeneration or in the worst-case its replacement, is related to the reversibility of deactivation [2]. Deactivation caused by poisoning, fouling and deposition of heavy compounds is generally reversible, and therefore regeneration is possible, while in the case of chemical transformation, thermal or mechanical degradations, deactivation is irreversible [3]. Poisoning by strong chemisorption of reactants or products and coke formation by cracking/condensation reactions are the main sources of catalyst deactivation. The chemical composition of coke depends largely on the nature of catalyst, the feed composition and the operating conditions especially temperature. The coke can be either graphitic or polyaromatic molecules more or less alkylated, and even functionalized [4,5]. The usual treatment for its removal is combustion in air [2], such as in fluid catalytic

cracking where coke is oxidized in a fluidized bed operating continuously.

The coke combustion forms initially water then CO₂ or CO [6]. The high exothermicity of combustion reactions (Eqs. (1)–(3)) and the limited thermal stability of most catalysts make difficult the control of the process temperature. Hot spots can appear (especially, where the coke is located) leading to irreversible damages i.e. metal sintering, zeolite dealumination. . .



To avoid a thermal runaway, a first solution consists in carrying out the combustion of coke in a fluidized bed reactor in two successive stages; the first stage being maintained at a low temperature just enough to burn hydrogen atoms and a part of carbon atoms, while the second stage is maintained at a higher temperature to remove the more stable residual coke. This procedure is commonly used in fluid catalytic cracking process (FCC) [7,8]. Conventional operating conditions of a regenerator are: 950 < T < 1050 K and residence time between 5 and 10 min [2]. Another solution to limit the oxidation temperature and the regeneration time is to add a very small amount of noble metal (1 ppm Pt by example) to the coking catalyst, thereby ensuring complete combustion at lower temperature and minimizing the afterburning. Despite

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these improvements, zeolite modification (dealumination) during regeneration process is still an unresolved problem and part of deactivated catalyst must be replaced by fresh catalyst. In a FCC unit, the amount of catalyst used reaches 100–300 tons every 2 months [2]. Consequently, to limit the cost associated with catalyst replacement, the development of efficient and milder regeneration methods is of particular interest.

More expensive oxidizing agents such as ozone was used to remove coke from zeolites. With ozone-enriched oxygen, coke can be oxidized at a temperature lower than 523 K without risk of hydrothermal degradation. However, the use of this strong oxidant is limited because coke located in the core of extrudates cannot be removed due to the rapid dissociation of O₃ [8]. The half-life time of ozone in air at 523 K is only 1.5 s and is much more lower in the presence of heterogeneous catalyst. Moreover, the use of ozone in industrial processes should be avoided since ozone emission into the atmosphere is strictly controlled and could not exceed 75 ppb. N₂O is also a potential oxidizing agent, it is moreover cheaper than O₃ and is even produced as waste in adipic acid preparation. However, relatively high temperatures (700–800 K) are required for coke removal by nitrous oxide. Consequently, despite the interesting results obtained [9], the substitution of classical combustion processes under air by N₂O treatment seems very unlikely.

Among alternative techniques to overcome the difficulties associated with thermal regeneration, non-thermal plasma can be considered as a promising technology due to its non-equilibrium characteristics [10]. In such a plasma, highly energetic electrons are generated at atmospheric pressure and low temperature (room temperature), it leads to the formation of highly active species such as radicals, excited atoms, ions and molecules. The generated reactive species play important roles in the initiation and propagation of many physical and chemical reactions [11]. Under oxygen plasma, the most abundant species formed are the positive ion O₂⁺, the negative ions O⁻, O₂⁻ and O₃ [12]. Bibby et al. [13] reported for the first time in 1986 that Radio-Frequency oxygen plasma can be used to remove coke from the surface of ZSM-5 zeolite while the authors observed that internal coke was not eliminated. Khan et al. [14] showed that O-atoms obtained by O₂ dissociation in a glow discharge plasma can lead to the partial decoking of a zeolite. However, such a plasma can only be generated at pressures of the order of 10⁻³ mbar, which make the process little attractive for industrial applications. A dielectric barrier discharge (DBD) reactor operating at atmospheric pressure was used by Hafezkhiani et al. [15] to perform the decoking of Pt-Sn/Al₂O₃ catalyst. A complete carbon removal was obtained using argon as diluent gas with oxygen, but the structural properties of the catalyst was modified after the regeneration step: decrease of surface area and metal dispersion.

Consequently, there are needs to perform complementary studies on the use of non-thermal plasma for coke removal.

In this study, a Dielectric Barrier Discharge (DBD) plasma reactor with a pin to plate geometry was used. The coked zeolite was shaped as a wafer and placed into the discharge zone. The influence of the nature of gas (air or He + O₂), deposited power and treatment duration was investigated. Coke removal was determined using the classical method ATD-ATG, the textural and structural properties of zeolite were characterized after plasma treatment by surface area measurement, IR analysis (acidity). Moreover, it was possible to evaluate the efficiency of plasma treatment at the surface of the wafer using a CMOS camera and after image treatment by shades of grey.

Since some coke molecules, trapped in the pores of zeolite, can lead to the formation of radicals by spontaneous ionization [16], the 2D-EPRI spectroscopy was used to determine the localization of radicals in the disk [17]. This analytical technic is an interesting tool to understand how coke elimination occurs under the plasma

Table 1
Characterizations of fresh and coked zeolites.

	Unit	Fresh	Coked
Coke ^a	wt.%	0	6.5
Soluble coke		–	2.6
Insoluble coke		–	3.9
V _{micro} ^b	cm ³ /g	0.15	0.10
V _{meso} ^c		0.38	0.39
[PyH ⁺] ^d	μmol/g	242	158
[PyL] ^e		63	38

^aMeasured by ATD/ATG; ^bMicropore volume obtained by using t-plot method; ^cmesopore volume = V_{total} – V_{micro} (V_{total} determined from the adsorbed volume at p/p₀ = 0.99); ^{d,e}measured by pyridine adsorbed on Brønsted and Lewis acid sites after evacuation at 423 K.

discharge. To the best of our knowledge, such study has never been reported before.

2. Experimental part

2.1. Fresh and coked ZSM-5 zeolites

The material used is a hierarchical zeolite resulting from NaOH treatment of a commercial ZSM-5 zeolite with a Si/Al molar ratio of 40. The post-synthesis treatment is already described in ref [18]. Acid and textural properties are summarized in Table 1. The catalyst was coked in a micro-fluidised bed upon pyrolysis of oak at 773 K [19]. The coke content was measured with a SDT Q600 TA thermogravimetric analyser under a 100 mL/min flow of air up to 1173 K. Textural properties were determined by sorption measurements of nitrogen at 77 K, by Micromeritics ASAP 2000 gas adsorption analyzer. Micropore volume was calculated by using the t-plot method. Prior to the measurement, coked samples were outgassed at 363 K for 1 h. The FT-IR measurements were carried out in a Nicolet 750 Magna FTIR 550 spectrometer (resolution 2 cm⁻¹). Samples were shaped in thin disk (20–25 mg) with a diameter of 1.6 cm by using a manual hydraulic press (0.5 ton). The catalyst was activated in situ in the IR cell under secondary vacuum (10⁻⁶ mbar) at 423 K. 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 and by using extinction coefficients given in Ref. [20].

2.2. Coke composition

The coke molecules trapped in zeolite pores were recovered after digestion of the spent catalyst using a concentrated hydrofluoric acid solution (51 vol.%). One fraction of coke was soluble in CH₂Cl₂ (soluble coke), the other one insoluble (insoluble coke) led to black particles that can be recovered by a simple filtration, then weighted in order to determine its proportion. The soluble coke fraction obtained after CH₂Cl₂ evaporation was analyzed and quantified by GC-MS (Thermoelectron DSQ) and GC-FID (Agilent), respectively. The soluble and insoluble coke fractions were also 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. Sample preparations, analysis and calibration methods were done by following the same methodology described in Ref. [21].

2.3. Pin to plate DBD reactor

The reactor used to generate the plasma discharge was a Dielectric Barrier Discharge (DBD) type with a pin to plate geometry (Fig. 1). The disk (20–25 mg, φ = 1.6 cm ⇒ 2 cm²) is placed directly into the discharge at the surface of the dielectric material (glass).

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