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Differences among the deactivation pathway of HZSM-5 zeolite and SAPO-34 in the transformation of ethylene or 1-butene to propylene

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ABSTRACT

The deactivation of HZMS-5 and SAPO-34 catalysts has been studied in the transformation of ethylene and 1-butene under propylene intensification conditions. The deterioration of spent catalysts' physical properties have been quantified and coke has been characterized by TPO and by several spectroscopic techniques (Raman, ^{13}C NMR, FTIR, FTIR-TPO), in order to determine the effect reaction medium composition and the severity of catalyst shape selectivity have on the nature and location of the coke in the porous structure. The results reveal that the mechanism for coke deactivation consists of two steps: one for the formation of alkylated aromatics by oligomerization and another for the coke growth-condensation. The first step is analogous for both catalysts and it principally depends on the catalyst acid strength and acid site density. The second step is different for both catalysts: the microporous structure of SAPO-34, with cavities in the intersections, inhibits the diffusion of alkylated aromatics towards the outside of the structure, thus blocking active acid sites; whereas, HZSM-5 structure, with a high connectivity and without cavities, favors the diffusion of the aromatics that evolve for a longer time outside of the micropores. At process conditions, the results demonstrate that the coke formation is faster from ethylene than from 1-butene, due to the lower reactivity of ethylene for oligomerization-cracking mechanisms as well as its higher capability for coke formation.

1. Introduction

The increasing light olefin demand is boosting the intensification of conventional processes for its production from crude oil, by steam cracking and fluid catalytic cracking (FCC) [1,2], and from other fossil sources (natural gas, coal) by the MTO (Methanol to Olefins) process [3]. New catalytic routes from fossil fuels are currently at different developing stages, such as: (i) the transformation of DME (DTO process) obtained from natural gas or coal [4]; (ii) methane transformation (natural gas) via chloromethane [5]; (iii) coupled methanol-hydrocarbon cracking (CMHC) [6]. In addition, light olefin production is a priority goal in biomass valorization routes, by ethanol or bio-oil catalytic transformation [7–9] and in the valorization of polyolefinic plastic wastes [10,11].

Although the aforementioned processes are selective for light olefin production, they do not satisfy the increasing propylene demand (with an annual rate of 5.7%), due to the increase in the production of petrochemicals, such as polypropylene and acrylonitrile, among others [12]. Consequently, it is necessary: (i) to intensify propylene production, by using selective catalysts and by modifying the reaction conditions in light olefin production processes [13]; (ii) to explore olefin interconversion routes, by selectively transforming ethylene and butenes into propylene [14,15]. HZSM-5 catalyst is the most widely used for the production of propylene from different raw materials and is conventionally used as an additive in the FCC units for increasing light olefin yield [16].

The suitable kinetic performance of HZSM-5 zeolite is due to its crystalline three-dimensional structure, characteristic of pentasil family (MFI topology), configured by five tetrahedral rings, which form two types of channels that are perpendicularly crossed. These ellipsoidal channels, some straight (0.53 × 0.56 nm) and some in zig-zag (0.51 × 0.55 nm), are 10-membered ring openings [17]. This structure provides the HZSM-5 zeolite with a suitable balance between different properties: shape selectivity, acid strength of the sites, acid site density, crystalline channel interconnection and hydrothermal stability. Light olefin interconversion takes place by the well-established oligomerization-cracking mechanism [18,19], with secondary reactions of isomerization, cyclation, aromatization, together with the undesirable coke formation. In

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Nomenclature

Roman symbols

B/L	Brönsted/Lewis ratio
C_c	coke content (wt.%)
D, G	bands in the Raman spectrum
d_p	pore diameter (Å)
f_{c1}	fraction of coke type I (%)
F_i	molar flowrate of i lump in the product stream ((mol of C) h^{-1})
F_0 and F	butene molar flowrate in the feed and in the outlet stream ((mol of C) h^{-1})
G_p	position of G band (cm^{-1})
G_w	width of G band (cm^{-1})
La	in-plane correlation length (nm)
S_{BET}	BET surface area (m^2g^{-1})
S_m	micropore area (m^2g^{-1})
S_i	selectivity of i component (%)
V_m	micropore volume (cm^3g^{-1})
V_p	pore volume (cm^3g^{-1})
X	conversion (%)

Greek symbols

ε_L, ε_B	molar extinction coefficients (cm μmol^{-1})

order to intensify propylene production, as well as to attenuate deactivation by coke, several initiatives for HZSM-5 zeolite alteration have been suggested aimed to: (i) modifying the porous structure, by generating mesopores and/or hierarchichal structures by desilication or dealumination [9,20,21]; (ii) decreasing crystal size [16,22]; (iii) altering acidity by selecting a suitable SiO_2/Al_2O_3 ratio and by adding different compounds (P, K, La, transition metals) [23–27] and; (iv) incorporating the zeolite in a composite [28]. These modifications result in a decrease in the acid strength and acid site density, effective for increasing zeolite hydrothermal stability and for decreasing coke formation, as hydrogen transfer reactions are disfavored [9,29,30].

In the MTO process, industrially commercialized by UOP/Norsk Hydro technology, the SAPO-34 catalyst is used [31], of CHA topology, with big cages (0.67 × 0.11 nm) interconnected through small windows (0.38 × 0.38 nm) formed by 8-membered rings [32]. This porous structure allows forming poly-alkylated benzenes in the cages, which are active intermediates in the formation of light olefins from methanol, and furthermore, it restricts the diffusion of heavy and branched hydrocarbons in the narrow windows between the cages [33,34]. In order to increase propylene selectivity and extend the catalytic life (the main problem of this catalyst), several modifications of SAPO-34 have been studied, as are: (i) decreasing crystal size [35]; (ii) tuning acidity, by oxalic acid treatment or doping with Ce [36]; and, (iii) agglomerating it with ZrO_2 as a binder [37]; and, (iv) introducing hierarchichal pore systems via templating with carbon materials [38].

The modifications of HZSM-5 zeolite and SAPO-34 allow obtaining a high olefin yield, with high propylene selectivity. However, both catalysts (largely SAPO-34) show a rapid deactivation by coke, which justifies the growing interest in the knowledge of its formation mechanism. In this work the deactivation by coke of HZSM-5 zeolite and SAPO-34 catalysts has been studied in the transformation of 1-butene and ethylene, under suitable reaction conditions for intensifying propylene production. The combination of the results of catalyst properties deterioration and the nature of coke (studied by TPO, MS/FTIR-TPO, FTIR, Raman and ^{13}C NMR) pursue improving the knowledge about the effect of catalyst properties (particularly shape selectivity severity, which is different for both catalysts) and the composition of the reaction medium (which is different for the 1-butene and ethylene feeds) on the mechanism for coke formation. This study is supported on the literature knowledge about the mechanisms of coke formation on HZSM-5 zeolite and SAPO-34 catalysts used in other catalytic processes for olefin production, such as cracking [39–41] and the MTO process [42,43]. Moreover, it is based on previous knowledge about the spectroscopic analysis methodology of the coke deposited on acid catalysts [44–48].

2. Experimental

2.1. Catalysts

HZSM-5 zeolite was supplied in ammonium form by Zeolyst International ($SiO_2/Al_2O_3 = 80$), and was calcined at 570 °C to obtain the acid form. SAPO-34 (of composition $(SiO_2)_{0.08}$ $(Al_2O_3)_{2.8}$ $(P_2O_5)_{0.98}$ $(HCl)_{0.02}$ $(C_8H_{19}N)$ $41H_2O$) was prepared following the method of Lok et al. [49], with tetraethyl ammonium hydroxide (TEAOH) at 20 wt.% as template. The removal of the template was carried out by calcination in a muffle furnace at 575 °C for 6 h with a heating rate of 5 °C min^{-1}.

The catalysts were obtained by agglomerating the active phase (25 wt.%) by wet extrusion with bentonite (Exaloid, 30 wt.%) as a binder and alumina (Martinswek, 45 wt.%) as inert charge. This agglomeration is required in order to: (i) confer a suitable mechanical and hydrothermal resistance; (ii) obtain higher accessibility of the reactants to the active phase, and; (iii) attenuate deactivation by coke, since the coke deposition on the mesoporous matrix minimizes the blockage at the mouth of micropores [50]. The extrudates were first dried (110 °C, 24 h) and then were sieved to a particle diameter between 0.15 and 0.3 mm. Finally, the catalysts were calcined at 570 °C for 2 h. This treatment is required in order to achieve a balance of the acid sites, which allows keeping the catalyst hydrothermally stable and maintaining its kinetic performance throughout reaction-regeneration cycles [46].

The surface area and porous structure were measured by N_2 adsorption-desorption (Micromeritics ASAP 2010). The total acidity and acid strength of the catalysts were determined by monitoring the adsorption-desorption of NH_3, by combining the techniques of thermo-gravimetric analysis and differential scanning calorimetry using a Setaram TG–DSC calorimeter connected on-line with a Thermostar mass spectrometer from Balzers Instruments [51]. The Brönsted/Lewis (B/L) acid site ratio has been determined by analyzing the region of 1400–1700 cm^{-1} in the FTIR spectrum of adsorbed pyridine, which has been obtained using a Specac catalytic chamber connected on-line with a Nicolet 6700 FTIR spectrometer. The results have been determined from the ratio between the intensity of pyridine adsorption bands at 1545 and 1450 cm^{-1} and taking into account the molar extinction coefficients of both adsorption bands ($\varepsilon_B = 1.67$ cm μmol^{-1} and $\varepsilon_L = 2.22$ cm μmol^{-1}) [52].

Table 1 summarizes the physical and acid properties of the fresh active phases and catalysts (after agglomeration). SAPO-34 shows a higher BET surface and micropore volume in comparison to HZSM-5 zeolite. The catalyst micropore volume corresponds to the active phase (zeolite or SAPO), whereas the volume of meso- and macropores corresponds to the matrix of the catalyst