Deactivation dynamics of a Ni supported catalyst during the steam reforming of volatiles from waste polyethylene pyrolysis

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ABSTRACT

The valorization of waste high density polyethylene (HDPE) for hydrogen production has been studied in a two-step process, comprising pyrolysis and subsequent steam reforming of the volatiles produced in the first step. Particularly, this work focuses on the deterioration mechanisms (sintering and coke deposition) of the Ni commercial catalyst used in the second step, as it conditions the overall process performance. Pyrolysis of HDPE has been performed in a conical spouted bed reactor at 500 °C, and the catalytic steam reforming of the pyrolysis volatiles, in a fluidized bed reactor at 700 °C. Deactivated catalyst samples were recovered at different values of time on stream, and characterized using XRD, N_2 adsorption-desorption, SEM and TEM electronic microscopies, temperature programmed oxidation (TPO), Raman, FTIR and LDI-TOF MS spectroscopies. The results show that the deactivation is due to the sintering and encapsulation -by coke- of Ni. The former is inevitable within the current conditions, and the latter can be ascribed to the condensation of adsorbed precursors that evolve over time. Encapsulating coke is partially carbonized into filamentous coke with lower effect on catalytic deactivation and higher economic interest.

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1. Introduction

Plastic wastes are a great source of chemicals and fuels due to the following facts: (1) their world production shows a continuous increasing trend, registering a global production of 311 million tons in 2014 [1], (2) the subsequent dumping, generating a serious environmental problem due to their low biodegradability [2], and (3) their favorable chemical composition. Europe reached a plastic waste generation of 25.8 million tons in 2014, from which 30.8% went to landfill and 69.2% was used for recycling or incineration [1]. Polyolefins involved approximately 49% of the plastic demand, consisting of high density polyethylene, low density polyethylene and linear low density polyethylene (HDPE, LDPE and LLDPE, respectively) and polypropylene (PP). The USA registered a municipal plastic waste generation of almost 32 million tons in 2012 (63% polyolefins), from which 8.8% was recovered [3]. Taking this all into account, the valorization of waste plastics, and polyolefins in particular, turns out to be essential, in order to counteract this increasing worldwide consumption and its effects in the environment within the sustainable development [4].

Tertiary recycling of waste plastics by means of pyrolysis is considered the most attractive strategy to valorize these residues on a large scale in the consumer society [5,6]. Consequently, the pyrolysis of plastics has received great attention and acquired notable technological development [7,8]. Furthermore, pyrolysis units are relatively simple, respectful with environment and may be placed next to the collection and classification points of urban solid waste. On the other hand, the composition of products can be modified by incorporating acid catalysts to the pyrolysis reactor [9].

The studies on thermal or catalytic pyrolysis of waste polyolefins have been mainly targeting the monomer recovery [10–13] or the production of diesel fuel [14–16]. Pyrolysis of polyolefins at low temperature (500 °C) allows the selective production of pyrolysis waxes (C_{21+}) which can be fed into refinery units such as the catalytic cracker or the catalytic reformer, alone or together with the regular feed [17–19]. Besides, intending the production of monomers, the volatiles of the pyrolysis can be further treated with an in-line second step, such as secondary thermal cracking [20] or catalytic cracking [21–24]. The advantages of the sequenced two-step process are: (i) higher versatility when operating at the

optimum temperature in each step; (ii) lower catalyst deactivation in the second transformation, without the problems inherent to the plastic melting on the catalyst. These advantages of the sequenced two-step process are attractive for H_2 production, by means of in-line catalytic reforming of the volatiles exiting from the pyrolysis reactor. In a pioneer work with this strategy, Czernik and French [25] studied the continuous and sequenced polypropylene pyrolysis and volatile reforming, in separated fluidized beds, yielding 80% H_2 (with respect to the theoretical maximum) using a naphtha reforming commercial catalyst in the second reactor. Wu and Williams [26–31] and Acomb et al. [32] studied the performance of different reforming catalysts and conditions in this kind of sequenced pyrolysis-reforming of polyolefins. Furthermore, several authors [33,34] have employed fixed bed reactors in both steps. Erkiaga et al. [35], operating in continuous regime, proved the advantages of the conical spouted bed reactor (CSBR) in the first step of HDPE pyrolysis, due to the fact that the vigorous cyclic movement of sand particles covered by plastic avoids the bed defluidization. Moreover, the fast rate of mass and heat transport between phases allows obtaining a homogeneous volatiles stream consisting of C_{5+} hydrocarbons at low temperature (500 °C). These authors emphasize the limitation of the process due to the deposition of carbonaceous material (coke) in the reforming fixed-bed catalytic reactor. Barbarias et al. [36] have improved the system performance, using a fluidized bed reactor in the catalytic reforming step.

It is well stablished in the literature that deactivation of Ni catalysts in reforming reactions takes place due to coke deposition and Ni sintering. Several authors studied the evolution of coke content and nature in the reforming of hydrocarbons, such as methane [37,38] and propane [39], identifying two coke types: (i) Ni-encapsulating amorphous coke; and (ii) structured filamentous coke. The latter is sometimes called fibrillar or whisker-like coke and if the conditions are appropriate, it can be classified as carbon nanotubes (CNTs). Latorre et al. [40–42] proposed a mechanism of CNTs formation in which methane forms a metastable carbide, which releases carbon atoms that are diffused through the interphase of metallic nanoparticles, forming the nanotube after a nucleation stage. In the reforming of oxygenates, such as ethanol [43–46], dimethyl ether [47,48], and bio-oil [49], two main coke types were determined as well. In these works, the condensation of oxygenated reaction intermediates plays a major role in the rapid formation of amorphous and encapsulating coke, while the formation of structured coke is mainly due to CH_4 dehydrogenation and Boudouard reaction. All these works highlight the relevance of the feed composition and reaction conditions (temperature and steam/carbon ratio) on the content and nature of the deposited coke. These types of coke have been detected in the spent catalyst used in the production of hydrogen from polyolefins too [27,29–32]. On the other hand, it is well stablished that sintering is a noticeable deactivation cause in Ni catalysts, above temperatures in the range of 600–700 °C, depending on the catalyst structure, the operating conditions and the reaction medium composition [49–53].

This work focuses on the mechanisms of catalyst deactivation used in the second step of the sequenced pyrolysis-reforming of HDPE for hydrogen production. For this aim, we have used the same system used by Barbarias et al. [36] analyzing the evolution of catalyst and coke morphology at different stages of deactivation (values of time on stream). The dynamics of catalytic deactivation has been studied by means of X-ray diffraction (XRD), N_2 adsorption-desorption, scanning and transmission electron microscopies (SEM and TEM, respectively), temperature programmed oxidation (TPO), Raman spectroscopy, Fourier transformed infra-red (FTIR) spectroscopy and laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS). The optimized operational conditions

Table 1
Mass composition (wt%) of volatiles from HDPE pyrolysis.

Fraction	Compound	Yield (wt%)	Fraction	Compound	Yield (wt%)
C_1–C_4		1.50	C_{12}–C_{20}		25.64
	Methane	0.03		Diolefins	3.22
	Ethane	0.06		Olefins	13.07
	Ethylene	0.08		Paraffins	9.35
	Propane	0.08	Waxes		67.00
	Propylene	0.50		Light (C_{21}–C_{40})	29.50
	Butanes	0.18		Heavy (C_{41+})	37.50
	Butenes	0.57			
C_5–C_{11}		5.86			
	Paraffins	0.34			
	Isoparaffins	2.50			
	Aromatics	0.28			
	Naftenes	0.19			
	Olefins	2.56			

for minimizing the impact of catalyst deactivation are suggested, together with a simplified mechanism of catalyst deactivation.

2. Experimental

2.1. Materials

The HDPE was provided by Dow Chemical (Tarragona, Spain) in the form of chipping (4 mm). The main properties are: average molecular weight, 46.2 kg mol^{-1}; polydispersity, 2.89; and density, 940 kg m^{-3}. The higher heating value, 43 MJ kg^{-1}, was determined by differential scanning calorimetry (Setaram TG-DSC-111) and isoperibolic bomb calorimetry (Parr 1356).

The reforming catalyst was provided by Süd Chemie (G90LDP catalyst) and its chemical formulation is based on NiO, $CaAl_2O_3$ and Al_2O_3. The catalyst has the form of perforated rings (19 × 16 mm) with a metallic phase of Ni supported on Al_2O_3, which is doped with Ca, with the NiO content being 14 wt%. This catalyst was ground and sieved to 0.4–0.8 mm, which is the suitable particle size to attain stable fluidization regime.

2.2. Operating conditions and composition of the reformed stream

Pyrolysis and in line steam reforming runs were carried out by continuously feeding HDPE in a bench scale plant, provided with a CSBR for the pyrolysis step and a fluidized bed reactor for the reforming step arranged in-line. A detailed description of the equipment has been previously reported elsewhere [36].

The operating conditions in the HPDE pyrolysis step are: 500 °C; HDPE inlet flow, 0.75 g min^{-1}; water flow, 3 ml min^{-1}; mass of silica sand, 50 g; sand particle diameter, 0.3–0.35 mm range. The steam reforming step of pyrolysis volatiles was carried out at the following operating conditions: 700 °C; space time, 16.7 g$_{catalyst}$ min g$_{HDPE}^{-1}$; steam/plastic mass ratio, 4 (steam/carbon molar ratio, 3.1). Table 1 displays the composition of the volatiles stream exiting the HDPE pyrolysis step, fed into the steam reforming step. It is noteworthy that the CSBR reaches complete conversion of HDPE into volatiles at 500 °C. The volatiles stream is mainly comprised of heavy waxes (C_{41+}, 37.5 wt%) and light waxes (C_{21}–C_{40}, 29.5 wt%), with a concentration of the fractions C_{12}–C_{20}, C_5–C_{11} and C_1–C_4 of 25.6, 5.9 and 1.5 wt%, respectively.

2.3. Characterization of fresh and used catalyst

The deactivation study was performed with runs at different time on stream values up to 185 min, with the aim of analyzing the catalyst in different deactivation degrees. The fluidized bed system