

Regeneration of naphtha reforming catalyst using DBD plasma system

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Abstract: Experimental results confirmed that DBD plasma was able to remove carbon from the coked Pt-Sn/Al₂O₃ catalysts. TPO analysis was used to confirm the removal of the coke. BET analysis and CO adsorption methods were used to determine the surface area, pore volume and metal surface area of the plasma regenerated catalysts. Finally the catalyst performance test was performed to show the catalyst activity after regeneration.

Keywords: Pt-Sn/Al₂O₃ catalyst, DBD plasma, naphtha reforming, catalyst regeneration

1. Introduction

Catalytic naphtha reforming units attract attention regarding the global high octane gasoline demand. This process is used to reconstruct the low-octane hydrocarbons to more valuable high-octane gasoline called reformat without changing the boiling point range. Catalytic reforming is also a primary source of aromatics that is used in petrochemical industry [1]. One of the principal catalysts in naphtha reforming process is Pt-Sn/Al₂O₃ that gives rise to high yields of products. In this process, deposition of coke on the catalyst is the main cause of deactivation [2]. This deactivation is reversible and regeneration of the catalysts is possible by thermal methods which eliminates the coke. In order to restore the catalyst activity, the regeneration process should be performed without any changes in the internal structure of the catalyst. The traditional petrochemical catalyst regeneration method that is a high-temperature oxidation process makes some changes in catalysts morphology, surface area, and porosity, which can reduce their active life time [3]. Therefore, irreversible changes in the internal structure of catalysts in conventional methods highlight the requirement of alternative techniques, which is able to solve the thermal regeneration problem [4]. Another widely used method for catalyst regeneration is supercritical fluid extraction (SFE) [5]. In this method, high pressure used for catalyst regeneration makes some problems like difficulty in experimental set-up and may collapse the internal structure of the catalysts. On the other hand, regeneration time of the deactivated catalysts by conventional methods is a disadvantage compared to the novel methods such as plasma regeneration. According to what was mentioned above, the plasma-treatment method as a developing method in the field of catalyst regeneration [6] could regenerate deactivated catalysts at low temperature and pressure without any internal destruction [7].

The present study investigates pin-to-plate DBD plasma effect on the regeneration of Pt-Sn/Al₂O₃ catalyst. This plasma contains a number of reactive species, all of which could contribute in different proportions to the whole

decoking process. Catalyst regeneration with the plasma method was done at lower temperature and pressure than thermal regeneration method and the regeneration time was also lower than conventional methods, that is, in the order of several hours.

2. Experimental

2.1 Experimental materials

Both the fresh and coked catalysts were used as pellet (1.8mm in diameter), which was obtained from BouAli Petrochemical Plant, Iran. Also, the feed required for experimental runs was prepared from the industrial naphtha sample from Bouali Petrochemical Plant. The carbon content of the coked catalyst obtained by elemental analysis was 4.77% ±0.1%. In each experimental run, 1 g of coked catalyst was used.

2.2 Experimental set up

Fig. 1. Shows the experimental set up of the pin-to-plate dielectric barrier discharge (DBD). This reactor consists of a stainless steel wire electrode connected to a pin and a cylindrical brass electrode with a cross-sectional diameter of 4 cm and a height of 2 cm. The features of the power supply were 20 kHz frequency and 0-20 kV variable high voltage. The distance between the electrodes was variable from 1 to 3 cm with a 10 cm×10 cm×2 mm quartz plate as a dielectric. A Pyrex tube (2 cm diameter) was also used as a holder of the coked Pt-Sn/Al₂O₃ granules on the quartz dielectric. Argon and oxygen were applied as feedstock working gases. The optical fibre was placed in front of the Pyrex tube to collect the emitted light from the discharge for OES analysis. To record the electrical parameters, such as the output voltage and consumption power, a high voltage (HV) probe was adjusted to the supply electrode and a current probe was adjusted to the grounded electrode. In this experiment, the effect of Ar-O₂ pin-to-plate DBD plasma on coked Pt-Sn/Al₂O₃ catalysts in 5 minutes regeneration was investigated.

The applied voltage was approximately 13 kV and the distance between the powered and grounded electrode was 2 cm. The flow rates of Ar and O₂ as working gases

was adjusted on 250 cm³/min and the total flow was 500 cm³/min.

The experimental conditions in the DBD plasma were chosen in order to reach the appropriate results.

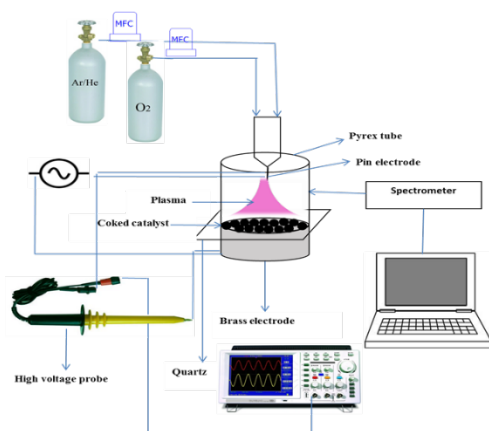


Fig. 1. Schematic diagram of a pin to plate DBD reactor

It is worthy to notice that the catalyst temperature in the considered plasma system did not exceed 350 °C. The plasma regeneration temperature was about 300-350 °C

In atmospheric pressure plasma systems, O₂ molecules are not ionized easily; therefore a noble gas must be applied to enhance the ionization rate [8]. Thus, argon was used in the DBD system.

2.3 Catalyst evaluation set-up

The schematic diagram of the catalyst evaluation set-up is shown in Fig. 2. The activity of the fresh and DBD plasma regenerated catalysts in the naphtha reforming reaction was evaluated by means of this experimental reactor system. After preparing the unit, 50 ml of the sample was placed in the reactor bed. Then the reactor system was purged with N₂ at 20 bar. In this condition the system pressure drop was checked during 5 hours to make sure about no leak in the connections, valves and measuring elements. Then the reactor system was purged with H₂ at 20 bar and the pressure drop was checked regularly. After that, N₂ was introduced to the reactor by the flow rate of 22.8 lit/h at the atmospheric pressure.

The temperature of catalyst bed was increased to 430 °C at the rate of 10 °C/min. After establishing the steady state conditions, a stream of high purity H₂ (360 ml/min) was introduced to the reactor for 5 h at the pressure of 5.1 bar. The H₂ flow rate was increased to 29 nlit/h during 0.5 hour and the temperature was raised to 470 °C at rate of 0.5 °C/min. In this temperature the naphtha feed at rate of 78 ml/h was introduced to the reactor. After 0.5 hour from introducing the feed, temperature was raised to 490 °C at rate of 0.5 °C/min. After that the sample was collected every 12 hours (10 samples). The effluent was analyzed by an on-line refinery gas chromatograph equipped by both TCD and FID detectors (Agilent 6890 n).

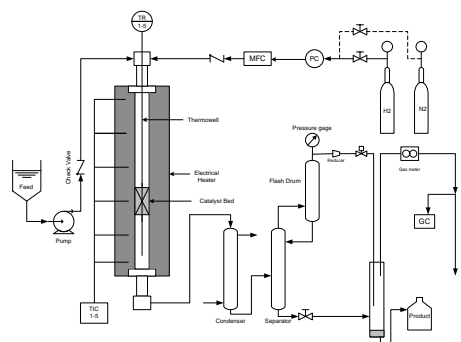


Fig. 2. Catalyst evaluation set-up

3. Results and discussion

3.1 Catalyst characterization

3.1.1 Optical emission spectroscopy (OES)

The main observed transition lines are listed in Table 1. The OES of the DBD Ar-O₂ plasma (O₂: 55 cm³/min, Ar: 440 cm³/min, voltage 13 kV, f= 20 KHz) showed transition lines with λ= 844.6, 777.4 nm related to oxygen atoms. In addition, there were multiple transition lines at λ= 738.4, 750.4, 763.5, 772.4 and 811.5 nm related to Ar*.

Table 1. Main transition lines observed in the optical emission spectra

Wavelength (nm)	Species	Transition line
750.4	Ar*	3s ² 3p ⁵ (² P _{1/2} ^o)4s-3s ² 3p ⁵ (² P _{1/2} ^o)4p
763.5		3s ² 3p ⁵ (² P _{3/2} ^o)4s-3s ² 3p ⁵ (² P _{3/2} ^o)4p
772.4		3s ² 3p ⁵ (² P _{3/2} ^o)4s-3s ² 3p ⁵ (² P _{3/2} ^o)4p
794.8		3s ² 3p ⁵ (² P _{1/2} ^o)4s-3s ² 3p ⁵ (² P _{1/2} ^o)4p
801.4		3s ² 3p ⁵ (² P _{3/2} ^o)4s-3s ² 3p ⁵ (² P _{3/2} ^o)4p
811.5		3s ² 3p ⁵ (² P _{3/2} ^o)4s-3s ² 3p ⁵ (² P _{3/2} ^o)4p
826.4		3s ² 3p ⁵ (² P _{1/2} ^o)4s-3s ² 3p ⁵ (² P _{1/2} ^o)4p
842.4		3s ² 3p ⁵ (² P _{3/2} ^o)4s-3s ² 3p ⁵ (² P _{3/2} ^o)4p
777.4	O*	2s ² 2p ³ (⁴ S ^o)3s ⁵ S ^o -2s ² 2p ³ (⁴ S ^o)3p
844.6	O*	2s ² 2p ³ (⁴ S ^o)3s ⁵ S ^o -2s ² 2p ³ (⁴ S ^o)3p

The reactive species, including O, O* and Ar*, could contribute in varying proportions to the whole decoking process. A general understanding has emerged that O atoms have a predominant role in this process. On the other hand, the production of effective O atoms was considerably enhanced by adding a noble gas, such as Ar, to the O₂ stream [8]. Apparently, collisions of energetic electrons with noble gas atoms initially excite noble gas atoms to higher metastable states. These high-energy metastable atoms subsequently transfer their energies to O₂ molecules, leading to their dissociation and the resulting production of O atoms, which is essential in the decoking process [4].

3.1.2 TPO analysis

Fig. 3 shows the TPO profiles of spent and plasma regenerated catalysts. The spent catalyst has a main peak in the interval of the 500-550 °C which is related to the coke on the support [2, 9]. This kind of coke can be removed easier from the catalyst surface. There is no

observable peak in the regenerated sample both at the low and high temperature. These results confirm that coke (carbon) was completely eliminated from the plasma-treated catalyst.

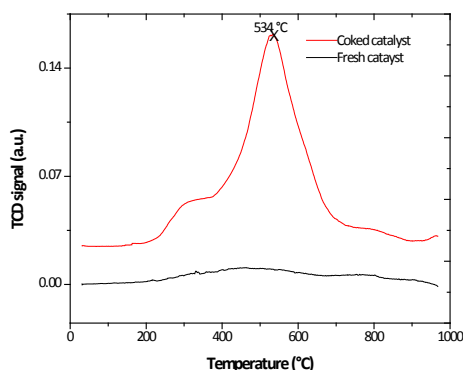


Fig. 3. TPO profiles of the coked and plasma-treated catalysts

3.1.3 The chlorine percent of catalysts

The chlorine percent of the fresh, coked, thermal and DBD plasma regenerated catalysts by XRF analysis were equal to 1.3, 1.2, 0.8 and 1.1 Wt.%, respectively. Comparison of the chlorine percent values reveals that the chlorine percent didn't so change in the DBD plasma regenerated sample and the chlorination process may be need after several regeneration processes compared with the thermal regenerated catalysts.

3.1.4 BET

The BET surface area and pore size volume of the fresh, coked (spent) and regenerated catalysts are summarized in Table 2. In this table, it can be observed that the surface area and pore volume of samples regenerated by the DBD plasma were approximately the same as the corresponding amounts of the thermal regenerated sample. These results indicated that the regenerated catalysts recovered their activities as well as the conventional methods.

Table 2. Carbon contents, specific surface areas and pore volumes of the fresh, coked, plasma and thermal regenerated catalysts

Sample	Surface area (m ² /g) ^a	Pore volume (cc/g) ^a	Carbon content (wt%)
Fresh	194.89	0.5539	0.00
Coked (spent)	131.42	0.4406	4.77
DBD Plasma regenerated	149.2	0.5202	0.00
Thermal regenerated	143.34	0.4896	0.019

^a Obtained by BET

3.1.5 Metal dispersion analysis (CO adsorption)

To better understand the Pt-Sn interaction, the Pt-Sn bimetallic phases were investigated through CO chemisorptions [10]. Table 3 presents the metal dispersion

ratio and metal surface area of the fresh, coked, thermal and plasma regenerated catalysts.

Table 3. Metal dispersion, metal surface area of the fresh, coked, thermal and optimum plasma regenerated catalysts by CO adsorption

Catalyst	Metal dispersion ratio (%)	Metal surface area (Sample*) m ² g ⁻¹	Metal surface area (Metal**) m ² g ⁻¹
Fresh	89.981	0.6889	222.21
Coked	2.6189	0.0258	6.4675
Thermal regenerated	76.903	0.5887	189.92
Plasma regenerated	79.442	0.5963	191.81

* Metal surface area based on 1 g of the sample

** Metal surface area based on the amount of sample containing 1 g of metal

The results show that 13.68% of the metal surface area is lost during the plasma regeneration process and about 14.53 % of the metal surface area is lost during thermal regeneration process. These results are also in good agreement with BET analysis results. The results also indicated that the metal content of the samples during the regeneration with plasma were remain without any change. Comparison between the crystal size of the fresh, coked and plasma regenerated catalysts that are about 1.25, 43.25 and 1.40 nm, respectively also indicated that sintering and pores collapse did not happen in the plasma regenerated sample.

3.2 Catalytic performance

In order to evaluate the catalytic performances, a naphtha cut was applied as feed to the reactor of experimental apparatus. This feed contains the paraffin, naphthenic and aromatic components which specified in Fig. 4.

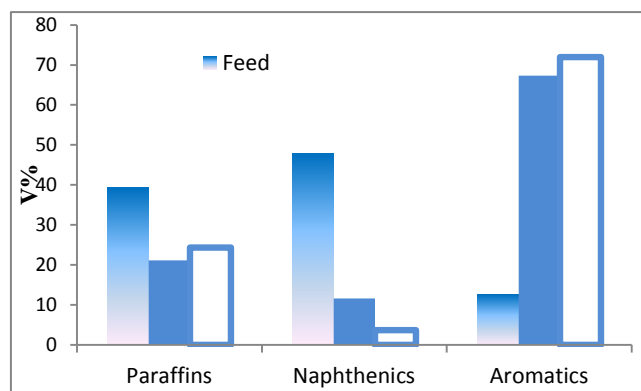


Fig. 4. Paraffin, naphthenic and aromatic contents in the feed, the product of fresh and DBD plasma regenerated catalyst

Reforming of naphtha feed was carried out in the reactor where a large fraction of normal paraffin and

naphthenic hydrocarbons converted to the aromatic components. As can be found from Fig. 4, the Pt-Sn/Al₂O₃ catalyst has good activity in the aromatic components production. The fresh catalyst can convert the feed (12.4 V% of aromatic contents) to the more valuable product with 67.31 V% of aromatic components. Also, c.a. 38% of paraffin contents in the feed were decreased over DBD plasma regenerated catalyst (from 39.3 V% to 24.33 V%). Comparing this paraffin content (24.33 V%) with that of the fresh catalyst (21.09 V%) indicates that DBD regenerated catalyst can convert paraffin components to the high octane number aromatic products. The naphthenic content in the output of reactor over the fresh and DBD plasma catalyst was about 11.6 and 3.70 V%, respectively. These results indicate that DBD plasma catalyst is more effective to production of aromatic components (Fig 4).

4. Conclusions

In the present study, we investigated the application of an atmospheric pressure pin-to-plate DBD reactor in the regeneration of the Pt-Sn/Al₂O₃ catalysts. TPO analysis, BET and OES were used for catalyst characterization. The results of the BET analysis indicated that the surface area and pore volume of the plasma-treated catalyst were not changed relative to the fresh samples. The results indicated that species such as O*, O and Ar* in the plasma environment had dominant roles in the coke oxidation process. The chlorine content of the coked, thermal and DBD plasma regenerated catalysts were determined by XRF analysis and the results revealed that the plasma regeneration process did not reduce the chlorine content of the sample significantly in comparison with thermal regeneration process. From CO adsorption analysis, the metal dispersion ratio for the fresh and plasma regenerated catalysts were equal to 89.98 and 79.44%, respectively. The metal dispersion analysis results showed that the metal distribution and the Pt-Sn interaction did not so change during the plasma treatment and therefore the activity of the plasma regenerated catalyst didn't alter so much during the plasma regeneration process. The catalytic activity tests indicated that over the DBD plasma regenerated sample c.a. 38 V% of paraffin contents in the feed was converted to the products. Aromatic content in the output of the reactor with DBD plasma regenerated catalyst was increased to 71.96 V% relative to 12.4 V% in the feed. In addition, aromatic content in the products over the fresh catalyst was about 67.31 V%. Also, the naphthenic content over the fresh and DBD plasma catalyst was about 11.6 and 3.70 V%, respectively. Compared to conventional thermal regeneration methods, the plasma regeneration of the coked catalyst is an innovative method that has no effects on the internal structure of the catalyst.

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