Catalysts Regeneration Using Laser Technique in Petroleum Industry

Adawiya J. Haider
Nanotechnology and Advanced Material Research Center,University of Technology/Baghdad
Khalid A. Sukkar
Petroleum Technology Department -University of Technology/Baghdad
Duha S. Ahmed
School of Applied Siecince/ Physis -University of Technology/Baghdad

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ABSTRACT

The catalyst cost regards one of the most important obstacles in petroleum industry. Therefore, the regeneration of catalysts could be more economic process to get high performance and low cost. In this work, three types of catalysts were investigated: Pt/A_2lO_3 (spent catalyst from reforming unit/Al-Doura Refinery), prepared $Pt/A_2lO_{3(Doura)}$ and Pt/HY. The performances of catalysts (activity, selectivity and catalyst stablity) were studied using n-heptane as feedstock under reforming conditions.

The operating pressure kept constant at atmospheric pressure, and the operating temperature 500 ^oC. The liquid flow was 0.4 l/h. The amount of catalyst was 50 gm, H_2/H.C ratio used was 2 for all experimental runs.

The catalyst of reforming process has been successfully regenerated using laser technique. This technique regards as a new approach for catalyst regeneration in petroleum industry to remove carbon deposits. On the other hand, this regeneration technique shows a great potential for economical processes in petroleum refineries. The results show that the best operating conditions for the regeneration process were: laser power of 13 watt and regeneration temperature of 650 ^oC. From the results of catalyst characterization it was concluded that the structures and morphology of all catalysts types did not effected or destroyed through using laser power.

Keywords: Petroleum industry; Catalysts regeneration by laser technique.

تنشيط العوامل المساعدة باستخدام تقنية الليزر في الصناعة النفطية

الخـلاصة

تعتبر كلف شراء العوامل المساعدة من اهم الصعوبات التي تواجهها الصناعة النفطية، لذلك فان عملية تنشيط العوامل المساعدة واعادة استخدامها تكون طريقة عملية لتحسين الاداء والجانب الاقتصادي. في هذا البحث تم دراسة ثلاثة انواع من العوامل المساعدة التي تستخدم في وحدات التهذيب : مستهلك من مصفى الدورة Doura pt/A2o3 ,pt/HY ,pt/A2 كعوامل مساعدة محضرة. حيث تم دراسة فعالية وانتقائية ومدى فقدان الفعالية لهذه العوامل المساعدة من خلال استخدام الهبتان

الاعتيادي كمادة اولية لتفاعلات التهذيب. أجريت التجارب تحت ضغط جوي اعتيادي ودرجة حرارة ٥٠٠^{o}C ومعدل جريان ٤ لتر/ساعة للهبتان و ٥٠ غم من وزن العوامل المساعدة ونسبة (HC/H_2) تساوي ٢ لجميع التجارب. اظهرت النتائج نجاح استخدام تقنية الليزر في تنشيط العوامل المساعدة المستخدمة في وحدات التهذيب، وتعتبر هذه الطريقة اسلوباً متطوراً لازالة الترسبات الكاربونية من سطح العمل المساعد في االصناعة النفطية. كما تعتبر هذه التقنية مجدية اقتصادياً في المصافي النفطية. اظهرت النتائج ان افضل ظروف التنشيط هي قدرة الليزر ١٣ واط تحت حرارة ٦٥٠ ^{o}C . من خلال دراسة مواصفات العوامل المساعدة تم الاستنتاج بعدم تأثر التركيب الداخلي والتركيب السطحي لجميع العوامل المساعدة المستخدمة في التجارب خلال تعرضها لاشعة الليزر.

INTRODUCTION

Catalyst deactivation can be defined as the main problem related to the loss of catalyst activity or selectivity with time on stream. Residuum reforming and hydroisomerization catalysts are susceptible to deactivation processes mainly caused by coke formation [1, 2]. The gradual buildup of coke in the catalyst eventually plugs the pores and deactivates the catalyst surface and lead to reduce the product yield and quality. On the other hand, replacing deactivated catalysts represents a significant cost in petroleum refining because the high cost of catalysts. Equally important are the costs and potential liabilities associated with treating and disposing spent catalysts [1, 4, and 5].

Catalysts are widly used in petroleum refinery processes (such as: catalytic reforming, catalytic hydroisomerization, catalytic hydrotreating and other processes). These processes are usually carried out over bifunctional catalysts which consist mainly of a metal phase (platinum, rhenium, iridium, and tin) dispersed on an acidic support such as chlorinated alumina, sillca, and zeolites. Therefore, many types of modified catalysts are used in industry to improve the process activity, selectivity and catalyst stability [3, 6].

It is important to mention here that, these petroleum processes included chemical reactions that are accompanied by the formation of undesired carbonaceous compounds that deactivate the catalyst. This ‘‘coke’’ can have different crystalline structures, morphologies, and reactivities, depending on the specific reaction taking place and the reaction conditions [1, 5].

Most of the catalysts that have been investigated in literature [8, 9, and 10] were focused on improvement of activity and selectivity of these catalysts to desire reformate products. Mazzieri et al. [8] investigated the deactivation and regeneration of the metal function of Pt-Re-Sn/Al_2O_3–Cl and Pt-Re-Ge/Al_2O_3–Cl for catalytic naphtha reforming. It was concluded that the coke formation is the main resin for deactivation of reforming catalysts. Labourè et al.[9] used Nd:YAG laser to clean of limestone. They concluded that this method is very affected to remove all depositions. Bauerle [10] shows that the term laser cleaning denotes quite different fields: the removal of particulates and the extended contamination layers from solid surfaces by laser ablation.

It is important to mention here that many previous studies on catalyst regeneration using classical methods, such as, regeneration by hot gases or oxidation methods to remove carbon deposits [1, 4, 11, 12]. There is limited previous work has been focused on the use of laser techniques in regeneration of

catalysts in petroleum industry. In the present work, the catalyst regeneration in petroleum industry using laser technique is studied to aim at:

1- Catalysts performance and deactivation using catalytic reforming process conditions.
2- Catalyst regeneration process using laser technology.

EXPERIMENTAL WORK

1- The Catalysts Performance and Deactivation

Catalysts and Apparatus: The catalysts performance and deactivation of reforming process was investigated using an experimental pilot plant as shown schematically in Figure (1). The apparatus consisted of a vertical tubular stainless steel reactor of 20 mm internal diameter, 30 mm external diameter and 680 mm height. The reactor was heated uniformly using an electrical furnace. The reactor fitted with accurate means for control of pressure, gas and liquid flow rates. The temperature at the reactor center of the catalyst bed was determined and controlled by a temperature control system, which have a calibrated thermocouple sensor type K (iron-constantan).

In the present investigation, high purity n-heptane (99.9%) was used. Pure hydrogen gas (99.98%) was supplied from Al-Mansour plant-Baghdad and Hexachloroplatonic acid H_2PtCl_6 (40%wt Pt) Germany supplier was used.

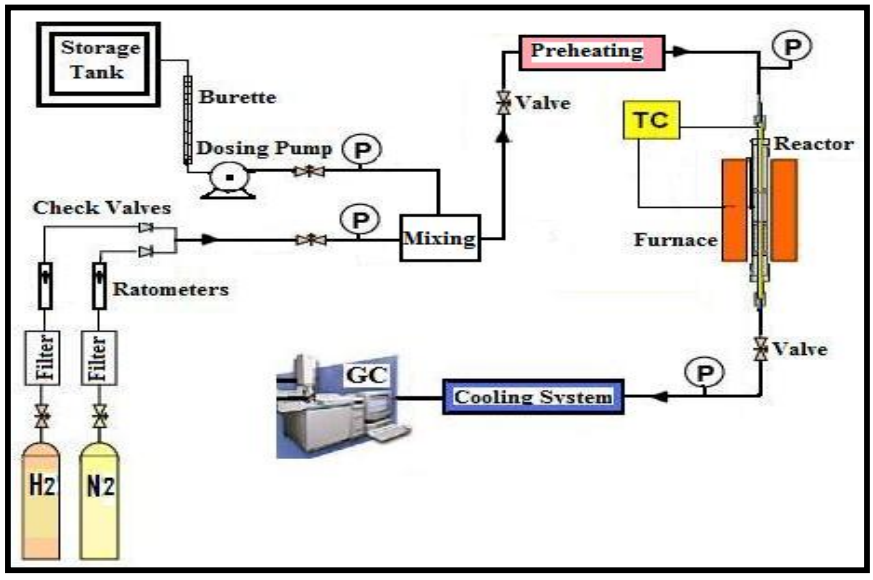

Figure (1) Schematic diagram of catalytic reforming apparatus.

Three types of catalysts were investigated: Pt/A_2lO_3 (Al-Doura Refinery), prepared Pt/A_2lO_3 and Pt/HY. All catalysts contain 0.5 weight parentage of platinum. The procedure of preparation is found in references [2, 4, 5]. The performance of catalysts (activity and stability) were studied using n-heptane as feedstock under reforming conditions.

Procedure: The prepared catalyst was dried at 110 °C in N_2 flow for 1 hour and then reduced at 450 ^oC in hydrogen flow for 4 hours. The operating pressure kept constant at atmospheric pressure, and the operating temperatures 500 ^oC. The liquid flow was 0.4 l/h. The amount of catalyst was 50 gm, H_2/H.C ratio used was 2 for all experimental runs [2, 11, 12]. The feed mixture of hydrogen and hydrocarbon was preheated to reactor temperature before entering the catalytic bed. For each run, the reformate products were analyzed in a Gas Chromatograph type Shimadzu GC-2014 with FID (Flam Ionizing Detector) using capillary column type S.G.E., length=25 mm, I.D.= 0.22 mm, film=0.2µm, and using nitrogen gas as a carrier gas.

1- Regeneration of Catalysts by Laser.

The deactivated catalysts were regenerated using laser radiation. The laser regeneration system is shown in Figure (2). The System consists from high power CO_2 laser (10-15 watt, and 10.6 µm JZ-3A), temperature indicator, and catalyst sample position to be regenerated (placed in rotated open glass container) [6, 7].

The regeneration process was done through exposure of the catalyst particles (50 gm of catalyst) to laser radiation at different intensities and time in present of air (O_2) as an oxidizing agent. The exposure time was varied between (1 to 4) minutes. Temperature indicator was employed to measure the local temperature generated through each exposure experiment.

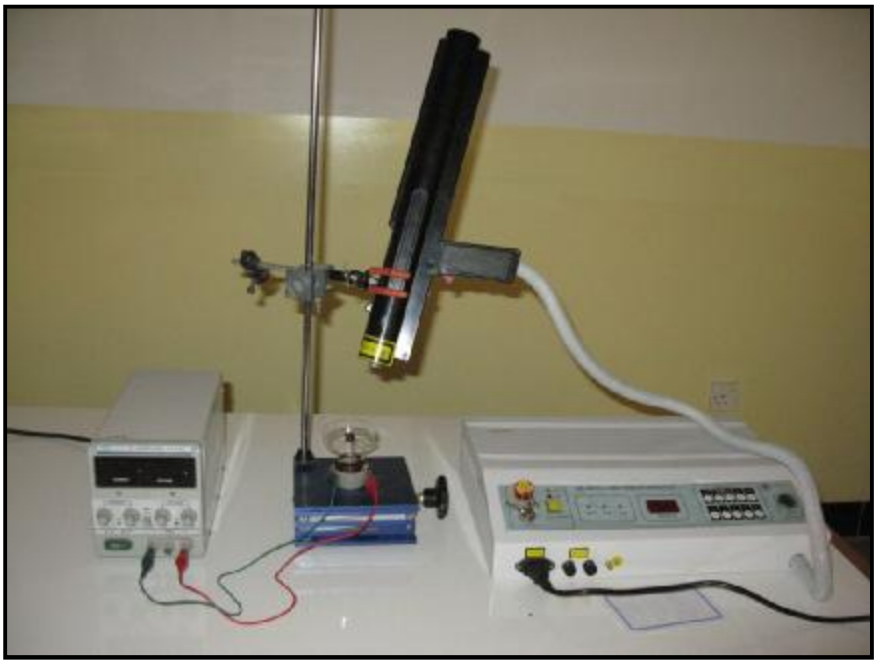

Figure (2) View of the laser system for catalyst regeneration.

RESULTS AND DISCUSSION

Catalyst Activity and Stability

Table (1) summarizes the general characterization and properties of original catalysts **($Pt/Al_2O_{3(Duora)}$, Pt/Al_2O_3 , and Pt/HY)** before use in reforming reaction. All types of catalysts are regenerated by hydrogen gas before use in reactor for 2

hours. Figure (3) shows the catalyst activity as function of reaction time. From this figure, it is clear all catalyst type loss their activity with time on stream. This is due to a continuous and slow build-up of various contaminants at the catalyst surface. The most common contaminants are the highly condensed hydrocarbon molecules "coke", in which it is formed by a series of side reactions. It was noted that the **Pt/HY** catalyst is more stable and deactivated more slowly than other types of catalysts (**prepared Pt/Al_2O_3 and $Pt/Al_2O_{3(Duora)}$)**. This is attributed to high surface area of zeolite catalyst (≈ 420 m^2/g). On the other hand, it was noted that, the prepared **Pt/Al_2O_3** gave the lowest activity in comparing with other types of catalysts as shown in Figure (3).

Table (1) Characterization of original catalysts before use or deactivation.

Property	$Pt/Al_2O_{3(Duora)}$	Pt/Al_2O_3 Prepared	Pt/HY Prepared
Platinum content (wt%)	0.5 wt% Pt	0.5 wt% Pt	0.5 wt% Pt
Surface Area (m^2/g)	250	280	420
Pore Volume (cm^3/g)	0.4	0.34	0.6
Average Pore Size (A^o)	100	25	20
Chlorine Content (wt%)	0.4	0.4	0.4
Internal (Si/Al)	-	-	1.6

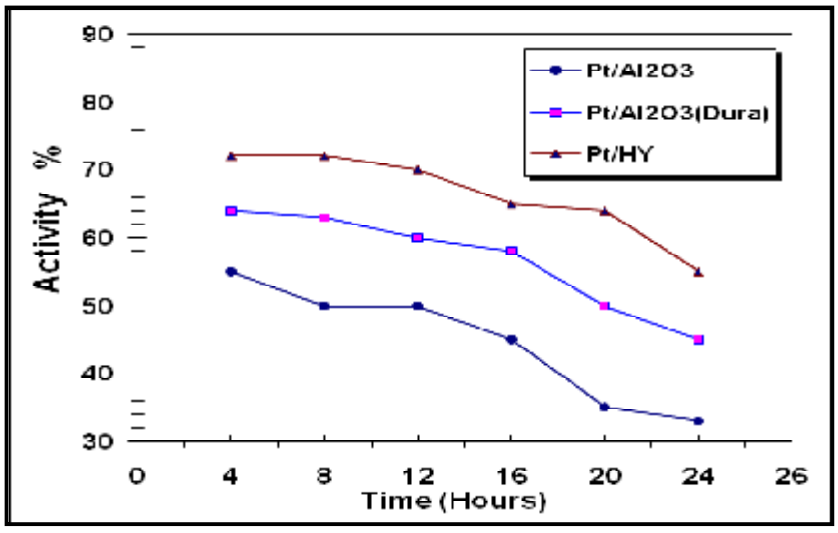

Figure (3) The relation between catalyst activity and reaction time.

In order to remove coke or carbon deposition from catalysts, a new approach for catalyst regeneration was suggested using a laser technique. The results indicated that the best operating conditions for the regeneration process by laser was with a 13 watt laser power and 650 ^{o}C regeneration temperature. This temperature makes sure that all carbon deposit will be converted to carbon monoxide and carbon dioxide with clean catalyst surface. On the other hand, the regeneration procedure was tested at different time of exposure ranging between 1-4 minutes. Depending on the monitoring of the regeneration process it was concluded that 3 minutes is the best time for catalyst laser exposure to remove the carbon from catalyst surface. It is important to mentioned here that, usually, laser cleaning is essentially surface treatment, where only a thin layer limited to a few microns or less than a micron is directly involved by absorption of light. But, in the present work the use of laser technique with high power lead to the cleaning of coke that included in all catalyst surface (all pores and internal textures). Such results are regarded to the high temperature that was generated through the catalyst laser exposure.

CATALYSTS CHARACTERIZATION AFTER LASER EXPOSURE

Table (2) shows the results of catalysts characterization after deactivation (subjected to reaction time of 24 hours) and after catalyst regeneration by laser power of 13 watt and 3 minutes of exposure time. It was concluded from this table that the catalyst surface area, the pore volume and the average pore size of all types of catalyst are stable and did not change with laser exposure. This indicated that the main characterizations of catalysts are stable and alter with radiation of laser. From these results, it is apparent laser regeneration technique of catalyst did not result in significant alteration of catalyst surface. The same conclusion was noted by Labourè et al. [9].

On the other hand, the cost of catalyst regards the most problem in petroleum refineries because the high price of new catalysts. Therefore, the regeneration of spent catalysts using laser technique will be contributed to lowering the cost of the process and then more economical processes.

Table (2) Characterization of deactivate catalysts.

Property	$Pt/Al_2O_{3(Duora)}$ Deact.	$Pt/Al_2O_{3(Duora)}$ Reg.	Pt/Al_2O_3 Deact.	Pt/Al_2O_3 Reg.	Pt/HY Deact.	Pt/HY Reg.
S.A. (m^2/g)	200	241	230	258	400	420
Pore Volume (cm^3/g)	0.3	0.4	0.3	0.34	0.3	0.5
Average Pore Size (A^o)	98	98	25	25	18	20
Chlorine Content (wt%)	0.3	0.3	0.21	0.21	0.32	0.3
(Si/Al) ratio	-	-	-	-	1.6	1.6

Figure (4) shows the catalysts activities that were reused after regeneration process by laser where the same reaction conditions were used. The result indicated that all catalysts are work well even when it exposed to laser radiation. This demonstrates the ability of catalyst to work again when it was subjected to laser

regeneration process. It was concluded from Figure (4), that the regenerated catalyst was active with about 90% of its original state. These results are in agreement with the work of Silvana et al. [3] and Jorge et al. [12].

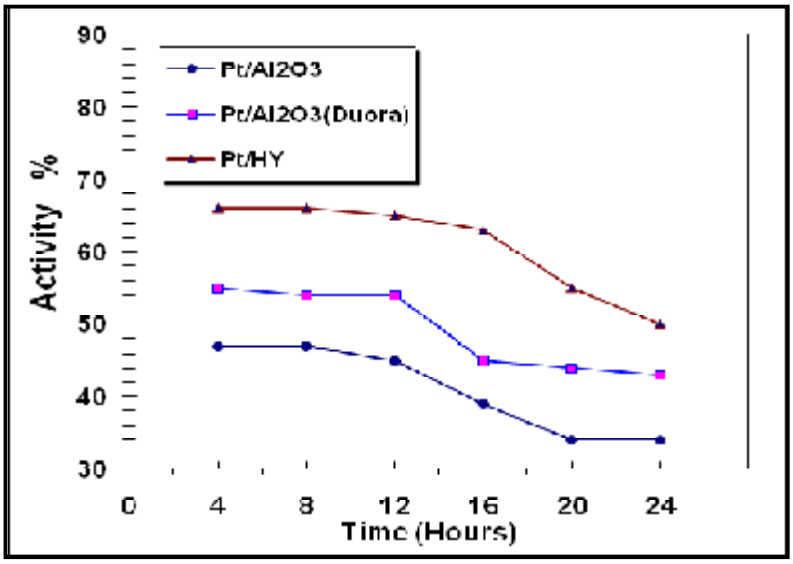

Figure (4) The catalysts activities of the reused catalysts after regeneration process by laser.

CONCLUSIONS

1- The catalyst of reforming process has been successfully regenerated using laser technique. This technique regards as a new approach for catalyst regeneration in petroleum industry to remove carbon deposits.
2- This kind of regeneration technique showed a great potential for economical processes in petroleum refineries.
3- It was concluded that the best operating conditions for the regeneration process were 13 watt of laser power and 650 ^{o}C of regeneration temperature.
4- The characterization results indicated that the structures and morphology of all catalysts types did not effected or destroyed or exchanged through laser exposure.

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