



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Kinetics of De-coking of Spent Reforming Catalyst

¹R. Ahmed, ²C.M. Sinnathambi and ¹D. Subbarao

¹Department of Chemical Engineering,

²Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

Abstract: Kinetics of decoking of spent reforming catalyst has been studied using a Thermo Gravimetric Analyzer (TGA) in presence of N₂ and air. It is found that the major portion of the coke species was hard coke which has activation energy equal to 86.3 kJ mol⁻¹. Slow heating rate and appropriate temperature are monitored to optimize the de-Coking process. Fourier Transform Infrared spectroscopy (FTIR) analysis has been applied to study the structure of coke deposited on supported metal catalyst (soft coke).

Key words: Kinetics, de-coking, TGA, FTIR, reforming

INTRODUCTION

The studies on carbon deposition as a factor of deactivation of naphtha reforming catalysts cover a broad spectrum of problems. It can start from the role of coking in catalyst degradation and extending further to the influence of numerous process parameters on the rate of carbon deposition and its mechanism. This includes the nature and morphology of coke deposits, their quantity and distribution between metal clusters and the support (Bartholomew, 2001). Coke can either chemisorbs strongly as a monolayer or physically adsorbs in multilayers and totally cover a metal particle and thereby completely deactivate the particles. It may also build-up in pores to the extent that they can stress and fracture the support material. In monometallic catalysts, the coke is usually deposited in the vicinity of the active metal sites or sometimes in wider pores of the catalyst without filling the entire the pores. As a result, the mean pore diameter shifts towards lower values after coking (Jovanovic and Putanov, 1997). It was reported by Antos *et al.* (1995) later by Menon and Paa (1997) that the location of coke (on the metal or on the support) and the nature of coke (light or graphitic) become more important parameters for catalyst stability than coke content. Regeneration of a spent catalyst is influenced by a great number of parameters. These are related to the mechanisms of deactivation, experimental regeneration conditions, and textural properties of the catalysts and the nature of the metallic phase. Therefore, the regeneration of a given catalyst must be treated as a particular case, and must take into account the history of the sample (purity, composition of feedstock, industrial conditions of

use, etc.). Furthermore, regeneration only makes sense in cases where deactivation can be reverted, as in the case of coke deposition (Afonso *et al.*, 1997). Temperature is probably the most critical parameter in a re-generation process because it influences directly the stability of the metallic phase and of the support. In addition to destructuring of the metallic phase Sinterization (agglomeration, crystallization, volatilisation), of the support and reaction of the catalytic phases themselves or with the support (thus forming inactive species) may occur.

These reactions normally take place at high temperatures (above 500°C). Catalysts deactivated by coke formation can be regenerated by burning off the coke. The combustion is typically carried out in diluted air, but in some cases partial coke removal is achieved with hydrogen or inert gases (Keskitalo, 2007). In study of the nature of coke in zeolite, which was established following the method, consists of dissolving the catalyst with a solution of hydrofluoric acid as suggested by Chen and Manos (2004), Guisnet *et al.* (1991) and Magnoux *et al.* (2006).

Coke molecules, generally formed and trapped in catalyst micropores, are recovered in dichloromethane (soluble coke) and GC/MS coupling or MS, UV-VIS determines their nature, distribution and IR as reported by Wang (2007). FTIR was used to analyze the structures of adsorbed molecules on a catalyst surface. The soluble components and it has applicability in investigating the structure of carbon deposits on supported metal catalysts. The other insoluble, composed of highly polyaromatic compounds, can be analyzing by Thermo Gravimetric Analysis (TGA) Ortega *et al.* (1997). The

coke formed on the catalysts, how it affects the catalytic activity, and the burning of the coke from a commercial coked catalysts by TGA technique is discussed in this work. TGA analysis carried in air and pure N₂ offers additional insights the chemical reactivity of the coke and gas solid regeneration kinetics. The current TGA method used here considers only the weight loss by coke burning in air at high temperatures. The kinetics study of de-coking assumed the coke removal by first order according to Ren *et al.* (2007). The soft coke nature is described by FTIR technique. The catalyst chosen for this experiment is an industrial spent Pt/Al₂O₃ naphtha reforming catalyst collected after the sixth cycle of operation in a commercial radial flow reactor unit at hydrocarbon pressure of 6 kg cm⁻², temperatures from 490 to 520°C, WHSV= 2.0 h⁻¹ and 3.8 H₂/HC molar ratio.

MATERIALS AND METHODS

Thermo Gravimetric Analyzer TGA: The spent catalyst collected from a commercial unit was finely ground and a sample of 5-10 mg was placed in the pan of the Perkin Elmer Pyris 1 TGA unit. The coked sample was thermally pre-treated starting from 50 till 200°C pure N₂ gas with a flow rate of 20 mL min⁻¹ to remove moisture and unbounded volatile material.

After this stage the pure N₂ gas was switched to air and heated to a preset maximum temperature of 800°C but maintaining the same flow rate. The weight loss with time at a fixed heating and flow rate was recorded to evaluate the kinetics of de-coking.

The mass fraction of coke precursors removed from coked catalyst at any time (t) is:

$$F_c = \frac{A_0 - A_t}{A_0 - A_f} \quad (1)$$

Where:

A₀ = Weight of sample after desorption of water and volatile compounds

A_t = Weight of sample at any time (t)

A_f = Weight of sample after de-coking

Fourier Transform Infrared spectroscopy (FTIR): The structure of adsorbed molecules and carbon deposits or soft coke on supported metal catalysts is determined by using FTIR technique as suggested by Li *et al.* (2000). The soft coke is determined by SHIMADZU FTIR 8400S instrument under controlled atmospheric conditions. 50 mg catalyst sample was ground in an agate mortar and mixed well with KBr (potassium bromide) power. The

product was pressed into a self-supporting disc at 9000 psi. The prepared sample disc was then placed in the centre of the reaction chamber, fixed in between a folded tungsten grid. Then the spectra are recorded by SHIMADZU FTIR spectrometer.

RESULTS AND DISCUSSION

Thermal Gravimetric Analysis (TGA): Figure 1 shows the TGA graph for a heating rate of 10°C min⁻¹ and flow rate 20 mL min⁻¹. The actual and differential weight losses from 50 to 800°C were recorded and presented in the figure. Initial weight loss under nitrogen flow up to 200°C (about 36 % of the total contaminants or deposits) was essentially due to the removal of water and volatile materials (Wang, 2007). The weight loss from this stage will not be taken into account for coke calculations.

For the temperature range of 200 to 800°C, the flow was switched from nitrogen to air with the same rate of heating and flow. The weight loss during this period is due to de-coking process and three distinct stages are observed. Rate of weight loss is in the 2nd stage from 400 to 600°C is higher than in the 1st stage from 200 to 400°C and the 3rd stage from 600 to 800 °C. This may be due to the nature of coke.

Matusek *et al.* (2000) distinguished three types of carbonaceous deposit on Pt/Al₂O₃, one on metal particles and one on metal-support perimeter and one entirely on the support.

In the first stage, the reaction rate of coke, termed as soft coke, is slow. The weight loss here is about 1.67 or 31.7 % of the total coke present in the spent catalyst as can be seen by Table 1 (heating 10 °C min⁻¹). As the temperature increases from 400 to 600°C (stage 2) a high with rapid weight loss of 3.31 % is observed (Table 1). This weight loss is due to higher rate of reactions by increasing the temperature and is called 'hard' coke. This indicates that the major form of coke deposit on the spent catalyst is hard coke which can be removed with proper de-Coking methods. This represents 62.8% of the

Table 1: Individual (Ind) and total weight loss in (TGA) de-coking, presented in weight percentages at heating rates (10 °C /min, and 15 °C /min) and at various temperatures range

Temperature range (°C)	Weight lost %			
	Heating rate 10°C min ⁻¹		Heating rate 15°C min ⁻¹	
	Ind	Tot	Ind	Tot
50 to 200°C (volatile)	2.97	36	4.12	44
200 to 400°C ('soft')	1.67	64	1.65	56
400 to 600°C ('hard')	3.31	64	3.14	
600 to 800°C (laid)	0.29	64	0.48	
Coke cumulative	5.27		5.27	

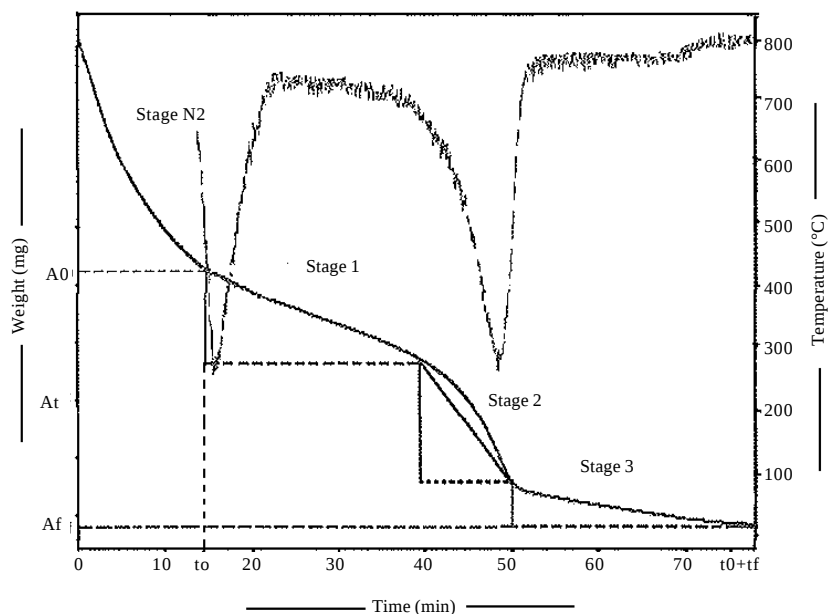


Fig. 1: Original TGA curve; shows the catalyst weight (mg) versus the time (min) and temperature ($^{\circ}\text{C}$) at heating rate $10^{\circ}\text{C min}^{-1}$.

total coke analysed on the spent catalyst. From 600 to 800°C (stage 3), reaction rate declines, either due to its non-reactivity or difficulty of coke left over deep in the catalyst particles. The non volatile or laid coke here represents 0.29 or 5.5% of the total coke. From the above observation it can be seen that the major portion of the coke material is hard coke represent double the amount of both the soft and non-volatile coke material.

Table 1 represents average percentage removal of foreign matter present on the industrial spent catalyst. The removal of coke was studied on the basis of heating rate. Two heating rate were chosen i.e. 10 and $15^{\circ}\text{C min}^{-1}$. This experiment was carried out in the same manner as TGA method discussed above. This study is conducted to quantify the importance of heating rate of coke removal. The loss in weight from the spent catalyst is calculated on a percentage basis. Based on the results from Table 1, it can be seen that the rate of removal of volatile matter and volatile materials is much better at higher ramp rate ($15^{\circ}\text{C min}^{-1}$) as compared to the lower rate ($10^{\circ}\text{C min}^{-1}$). As for the Weight loss from TGA analysis for coke material it can be seen that the removal soft coke is not influenced by the 2 different rates, but the efficiency for the 'hard' coke increases for the lower ramp rate.

For the laid coke, higher ramp rate is preferred. It is interesting to see that the cumulative or sum of coke (soft, hard and laid) species removal are similar for both rates.

Table 2: Quantification of normalised coke species at heating rates $10^{\circ}\text{C min}^{-1}$ and $15^{\circ}\text{C min}^{-1}$

Coke species	Normalized wt % of coke	
	Heating rate $15^{\circ}\text{C min}^{-1}$	Heating rate $10^{\circ}\text{C min}^{-1}$
Soft	31.7	31.3
Hard	62.8	59.6
Laid	5.5	9.1

From these observations it can be concluded that a lower ramp rate is much more preferred for regeneration studies since the major portion of the coke are the 'hard' type. This observation is in agreement with most industrial application. It was be noted by Afonso *et al.* (1997) that the slow heating rate are usually employed to better control the coke combustion.

Table 2 was an extension of Table 1. In Table 2 the results are normalized with the 3 different cokes present (ignoring the volatile materials). From this table it can be seen that the most abundance coke species are hard coke and their presence is about twice that of the other two (soft and laid coke).

For the present study the order of desorption of coke from the catalyst surface is assumed as 1st order. This is based on the studies by Querini and Fung (1997) and Ren *et al.* (2007). They looked at coke as tri-dimensional structure.

Coke exhibits a reaction order increasing from close to zero to approaching 1 as the oxidation reaction proceeds. This is because reaction is a gas-solid reaction

and it is proportional to solid surface area. Large surface coke particles decrease in size very slowly (reaction order for coke close to zero) at the early part of the burning order to generate similar surface area coke particles (reaction order for coke approaches 1). Based on these assumptions by Larsson *et al.* (1996) and Querini and Fung (1997) those of a kinetic model with respect to coke were adopted.

The results from TGA with a heating rate of $10^{\circ}\text{C min}^{-1}$ were fitted to their model and the following equation was used for the calculation of activation energy.

$$\frac{dc_c}{dt} = k_r c_c p_{O_2} \quad (2)$$

$$h = \frac{dT}{dt} \quad (3)$$

$$x = 1 - \frac{c_c}{c_c^0} \quad (4)$$

$$k_r = k_0 \exp\left(\frac{E_r}{RT}\right) \quad (5)$$

The integrated form is:

$$\ln\left[-\ln\left(\frac{1-x}{T^2}\right)\right] = \ln\left[\frac{k_0 p_{O_2}}{h \frac{R}{E} \left(1 - \frac{2RT}{E_r}\right)}\right] - \frac{E_r}{RT} \quad (6)$$

Where:

- C_c = Coke concentration
- C_{c^0} = Initial coke concentration
- E_r = Activation energy
- h = Heating rate ($^{\circ}\text{C min}^{-1}$)
- k_r = Rate constant
- k_0 = Pre-exponential factor
- p_{O_2} = Partial pressure of O_2
- R = $8.314 \text{ J mol}^{-1} \text{ }^{\circ}\text{K}$
- T = Temperature at time t
- X = Coke conversion

Therefore, a plot of $\ln [-\ln (1 - X)]/T^2$ vs. $1/T$; the slope gives the value of E_r and k_0 from the intercept.

The results from the above calculation are tabulated in Table 3. This current work further examines the exact Mechanism of coke removal through TGA experiments with two different heating rates for estimating the apparent activation energy of the process.

Table 3: Activation energies and pre-exponential factors for three stages in TGA run at $10^{\circ}\text{C min}^{-1}$

Stage	$E_r \text{ KJ mol}^{-1}$	k_0	Reaction range ($^{\circ}\text{C}$)
1	19.7873	1.80	200-400
2	86.3326	1.410^5	400-600
3	6.08098	-0.06	600-650

Ortega *et al.* (1997) method was used to estimate the activation energies. The highest activation energy was observed in stage 2 which is basically made up of 'hard' coke. It was demonstrated by Wang and Manos (2007), that relatively high apparent activation energy values should indicate decomposition as a chemical activated process, whereas low values should indicate diffusion limitation.

It was mentioned that the coke with a high H/C ratio has high combustion reactivity and low activation energy value. This indicates that the soft coke has a high H/C ratio while 'hard' coke has lower H/C ratio (Ortega *et al.*, 1997).

Fourier Transform Infrared spectroscopy (FTIR): FTIR is a surface analysis technique used to identify functional groups with greater emphasis on unsaturated hydrocarbons (C=C bonds; and aromatics) in the spent catalyst. The main objective of this characterization is to ascertain the nature of coke species especially the soft coke. Figure 2 shows the FTIR spectrum of the spent industrial catalyst prior and after N_2 treatment. The coke liberated from the commercial spent catalyst shows some absorption bands in the range between 400 and 4000 cm^{-1} (Fig. 2).

From the same figure it can be seen that the main absorption band at 3448.49 cm^{-1} is due to OH-Pt bond and the shoulders at 1606.59 and 1637.45 cm^{-1} are possibly due to adsorption of olefin and aromatics on the catalyst metal surface (Pavia *et al.*, 2001; Ruixia *et al.*, 2003). This may indicate that the coke species found near the active metal are soft coke and it is mainly made up of unsaturated hydrocarbon and heavy aromatics.

The absorption band between 3000 and 2800 cm^{-1} these are assigned to aromatic and aliphatic rings Li *et al.* (2000), probably produced by polycyclic aromatics like chrysene.

These two absorption bands at 2854.45 and 2925.81 cm^{-1} were caused symmetric and asymmetric flexion vibration of the C-H bonds associated with CH_3 (Ruixia *et al.*, 2003).

Evidence from work by Karge *et al.* (1996) suggested that the absorption band at 1400.22 cm^{-1} is due to ethylene type polymers adsorption.

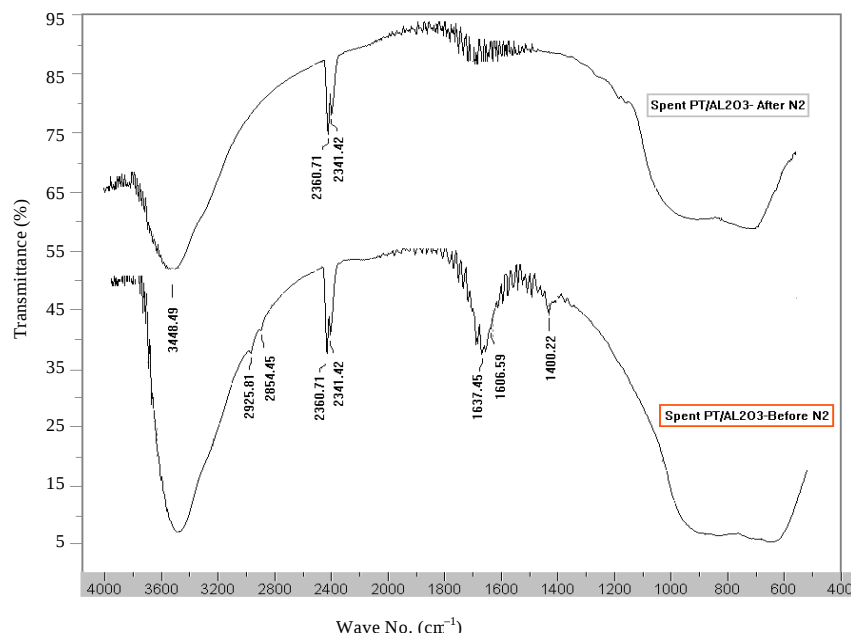


Fig. 2: FTIR spectrum for spent Pt/Al₂O₃ catalyst prior and after pre-treatment with N₂ gas

The results confirmed that, the commercial coked catalyst 3000 and 2800 cm⁻¹ is missing. This shows that eliminated of these coke precursors after treatment under N₂ gas is possible. So nitrogen gas might be used here to disrobe the coke precursors (soft coke) from the spent catalyst. This well documented by Chen and Manos (2004) and Wang and Manos (2007).

CONCLUSION

De-Coking process has been well described by TGA techniques. FTIR is used as evidence to show that soft coke can be removed after N₂ treatment. The 'hard' coke shown by the high activation energy of 86.3 KJ mol⁻¹ during TGA (second stage) is the most abundance species. The 'hard' coke can be removed by proper re-generation process because it is chemical control phenomenon, further heavier non-volatile coke is diffusion control in nature and its existence is minimal.

ACKNOWLEDGMENT

I would like to acknowledge chemical department technicians for their assistance, my colleagues and the catalysts group for their cooperative. Special thanks to Universiti Teknologi PETRONAS for their sponsorship.

REFERENCES

- Afonso, G.C., A.G.D. Aranda, M. Schmal and R. Frety, 1997. Regeneration of a Pt-Sn/Al₂O₃ catalyst: Influence of heating rate, temperature and time of regeneration. *Fuel Process. Technol.*, 50: 35-48.
- Antos, G.J., A.M. Aitani and J.M. Parera, 1995. *Catalytic Naphtha Reforming Science and Technology*. 1st Edn., Marcel Dekker, New York.
- Bartholomew, C.H., 2001. Mechanisms of catalyst deactivation. *Applied Catalysis A*, 212: 17-60.
- Chen, S. and G. Manos, 2004. Study of coke and coke precursors during catalytic cracking of n-hexane and 1-hexene over ultrastable Y zeolite. *Catalysis Lett.*, 96: 195-200.
- Guisnet, M., I. Neves, F.R. Ribeiro, C. Canaff, P. Magnoux and G. Perot, 1991. Coking, aging and regeneration of Zeolites. Xii-composition of coke formed on ushy during phenol alkylation with methanol-mode of formation. *Stud. Surface Sci. Catalysis*, 68: 735-743.
- Jovanovic, M.R. and P.S. Putanov, 1997. Nature and distribution of coke formed on mono-metallic platinum and bimetallic platinum-rhenium catalysts. *Applied Catalysis A*, 159: 1-7.
- Karge, H.G., W. NieBen and H. Bludau, 1996. *In-situ* FTIR measurements of diffusion in coking zeolite catalysts. *Applied Catalysis A*, 146: 339-349.

- Keskitalo, T., 2007. Modelling of chemical reaction kinetics with data from temperature-programmed experiments. Ph.D. Thesis, Department of Chemical Technology, Helsinki University of Technology.
- Larsson, M., M. Hulten, E.A. Blekkan and B. Andersson, 1996. The effect of reaction conditions and time on stream on the coke formed during propane dehydrogenation. *J. Catalysis*, 164: 44-53.
- Li, C.L., O. Novaro, X. Bokhimi, E. Munoz and J.L. Boldu *et al.*, 2000. Coke formation on an industrial reforming Pt-Sn/ γ -Al₂O₃ catalyst. *Catalysis Lett.*, 65: 209-216.
- Magnoux, P., A. Rabearitsara and H.S. Cerqueira, 2006. Influence of reaction temperature and crystallite size on HBEA zeolite deactivation by coke. *Applied Catalysis A*, 304: 142-151.
- Matusek, K., C. Kappenstein, M. Guerin and Z. Paal, 2000. Reactions of n-hexane on Pt-Sn/Al₂O₃ and removal of retained hydrocarbons by hydrogenation. *Catalysis Lett.*, 64: 33-36.
- Menon, P.G. and Z. Paa, 1997. Some aspects of the mechanisms of catalytic reforming reactions. *Ind. Eng. Chem. Res.*, 36: 3282-3291.
- Ortega, J.M., A.G. Gayubo, A.T. Aguayo, P. Benito and J. Bilbao, 1997. Role of coke characteristics in the regeneration of a catalyst for the MTG process. *Ind. Eng. Chem. Res.*, 36: 60-66.
- Pavia, D.L., G.M. Lampman and G.S. Kriz, 2001. *Introduction to Spectroscopy*. 3rd Edn., Harcourt College Publishers, Philadelphia.
- Querini, C.A. and S.C. Fung, 1997. Coke characterization by temperature programmed techniques. *Catalysis Today*, 37: 277-283.
- Ren, Y., N. Mahinpey and N. Freitag, 2007. Kinetic model for the combustion of coke derived at different coking temperatures. *Energy Fuels*, 21: 82-87.
- Ruixia, J., X. Zaiku, Z. Chengfang and C. Qingling, 2003. Characterization and performance of Pd-La/spinel catalyst for preparation of 2,6-diisopropylaniline. *Applied Catalysis A: General*, 250: 209-220.
- Wang, B. and G. Manos, 2007. A novel thermo gravimetric method for coke precursor characterization. *J. Catalysis*, 250: 121-127.
- Wang, B., 2007. Characterisation of coke precursors and acidity, product distribution. Ph.D. Thesis, Department of Chemical Engineering, College London University.