DEACTIVATION OF CATALYST DURING THE HYDROCRACKING OF VACUUM RESIDUE

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ABSTRACT

The effect of reaction time, as termed cycle-length on ~Mo W-Si-Al catalyst deactivation during hydrocracking of heavy vacuum residue as feed stocks was studied. Experiments were carried out in a stainless-steel high pressure autoclave reactor at constant pressure 60 bar, feed to catalyst ratio 10:1 and reactor temperature $425°C$. The time of the cycle-length was 4h, during which initial deposition of coke was observed as decreasing in the physical properties of the catalysts due to coke and heavy metals, deposition. The deposition of coke and heavy metals increases with the time of cycle-length, i.e by successive operating on the same catalyst sample and addition of the same feed. Catalyst deactivation during each cycle was monitored by changing in coke deposition and Ni and V on the catalyst and by carrying out activity tests on cumene conversion using pulse-reactor GC technique.

INTRODUCTION

The loss of catalyst activity is an important problem in the catalysis [Fogler, (1992)]. Many mechanisms have been proposed to explain the observed deactivation [Bott, et al. (1988)]. Fogler divided catalyst deactivation into three categories: deactivation by sintering , by coking or fouling and by poisoning [Lavens, (1972) and Bentlie & David (2000)].

Hydroprocessing catalysts are quite active for a number of important reactions [Edward & Franklin (1994)] such as hydrodesulfrization (HDS), hydronitrogenation (HDN) and, hydrodmetallation (HDM). For relatively light feeds, deactivation of the catalyst is minimal and the process can operate for long periods of time

before replacement of the catalyst. However, in hydroprocessing heavy residues, such as heavy vacuum bottoms which constitute a complex mixture of heavy compounds, mainly resins and asphaltenes with high molecular weight, low H/C ratio and high sulfur and metal [Ni-V] contents **[Koichi, et al. (2004)]**, catalyst deactivation can be sever, having an important commercial economic consideration with respect to catalyst life time .Also in residual oil hydroprocessing catalyst deactivation caused by coke deposition which in turn causes a serious problem **[Koichi, et al. (2004)]**. Coke mechanisms involving different routes, such as polymerization or condensation of coke precursors by the sever operating conditions. Asphaltenes presented in feed also deactivates the catalyst. Many researchers have found a direct relation between the amount of asphaltenes in the feed and deactivation of catalysts **[Higashi & Tacashi (2002) and Fujita et al. (2001)]**. Moreover, the quality of the asphaltenes often plays more important role than the quantity of asphaltenes in the feed **[Seki & Kamata (2000)]**. Coke deposition is known to be enhanced by product instability with the precipitation of asphaltens hydro processing reactions occur on the active sites of the catalysts therefore, a suitable pore size distribution is required to ensure the access of reactant molecules to the active site .A main reasons for deactivation of the catalyst involve, loss of active site **[Edward & Franklin (1994)]**. The aim of the present work is to describe the coke and feed metal deposition on the catalyst surface and their effects during hydrocracking on the activity of MoW/Si-Al catalyst using heavy residue.

EXPERIMENTAL

Catalyst:
   A commercial Mo-W/ Si -Al hydrocraking catalyst was used. It contains 3.98 wt % Mo and 3.75 wt % W as metal, loaded on synthetic silica alumina as support. The composition of catalyst is given in Table [1].

   Heavy vacuum residue (Gulf of Suez mix crude oil) was used as a hydrocracking feed stock and its characteristics are indicated in Table [2].

Table (1): Catalyst chemical composition.

Metal content , wt%	Content{%}
W	3.75
Mo	3.98
Al	15.04
Si	17.75

Table (2): Characteristics of vacuum residue feed stock.

Characteristics	Vacuum residue
Specific gravity {g/cm3} at70 °C	0.993
Flash point, °C	Over 320
Conradson carbon residue, wt%	18.75
Sulfur content, wt%	4.63
Asphaltene, content, wt %	6.4
Metals, ppm	
Ni	138
V	164.3

Experimental proceeding and analysis
Catalyst presulfiding

The catalyst was presulfided before carrying the hydrocracking experiments in a- static phase system [autoclave Parr type] **[Meroufy, et al. (2002)]**.

The reactions were conducted in a stainless high-pressure autoclave reactor [Parr-Model 4572], magnetically stirred, with an inner volume of 18000 ml and heated by digital controller. Reaction conditions were as follows: the required feed quantity and catalyst ratio, 10:1 [wt/wt], initial hydrogen pressure 60 bar, reaction temperature 425°C and process time 4h. After reached the required temperature and operated at the tested time [4h], the autoclave was maintained to cool to room temperature, and the total pressure decreased. The liquid and gas products were collected out of the autoclave and the catalyst was filtered and washed by solvent [naphtha]. The filtered catalyst was heated in an electric oven at 110°C for 2h, then cooled and a samples taken for analysis. The dried Catalyst re is loaded and mixed with a new sample of the feed stock to start a new run under the same operating condition.

The previous steps were carried out in 5 successive runs eash lasts for 4h, i.e ., the 5 runs take 20h runs which represent 4, 8 ,12 ,16 and 20 h. At the end of each run, sample of the tested of catalyst was taken off to be analyzed for carbon, metals and physical characteristics and their catalytic activity.

Activity-test

The catalytic cracking of cumene was performed by using micro reactor attached to a gas chromatograph [Perkin Elmer Sigma 3 m, with FID15. Reaction products were separated at 80°C in a 3.0m column packed with penton 34 with 5% diisodecylphtholate on Chromosorb WAW 35-80 mash .The conversion of the catalyst was determined at 400°C.

Analysis

- Metals analysis was made by atomic absorption spectrometer [Perkin – Elmer 800], while silicon was determined by gravemetric method.
- Surface area and average pore diameter of the catalysts were carried out using Quantachrome NOVA automated gas sorption system [model 2002].

RESULTS AND DISCUSSION

1- Effect of cycle-length on coke deposition :-

The quantification of the coke deposited on the surface of the catalyst during five cycles are summarized in Fig (1). This Fig indicates that the coke deposited increased with the operation time required to the 5 successive cycles. Meanwhile, the liquid distillate yield decreased and the yield of the residue increased..

In spite of the high hydrogen pressure applied (180 bar) during the reaction at 425°C, no catalytic efficiency towards cracking of the heavy residue was observed due to the complex structure of the feedstock and the rapid accumulation of coke through the successive cycles. With the start hydrocracking cycle, initial coking was observed causing the initial catalyst deactivation. The amount of coke deposited on the catalysts increased rapidly in the 1st cycle and reached about 8wt % .In the next cycles, the rate of coke deposition increased to 39wt% after 20h. this means that part of the formed coke was agglomerated in the feed and

the other was deposited on the surface of the catalyst [**Matsubite, et al. (2004)**].

The observed increase in coke formation during the operating cycles decreased the amount of liquid distillates produced during hydrocracking reactions (Figure 1). It means that the creaking activity of the catalyst decreased as the cycle-length increased and its selectivity towards producing liquid distillates was reduced. A self - poisoning phenomena was obtained due to the strong adsorption of coke species on the active sites of the catalyst [**Absi-Halabi, et al. (1999); Kriz, & Terman (1992); Trianm, et al. (1996) and Tanaka, et al. (1998)**]. The catalyst activity towards the conversion of the residue drops rapidly during the first cycle, then stays nearly constant for two-cycle, flowed by thermal conversion (noncatalytic) reactions.

2- Effect of cycle -length on the metal deposition :-

Fig (2) summarizes the metals (Ni,V) deposited on the surface of the catalyst during the operating cycle of hydrocracking of vacuum residue and indicated that both nickel and vanadium deposition increased with time due to the successive addition of fresh feedstock containing additional amounts of metals, Ni (138ppm) and V (1643ppm). Therefore, the main causes of the deactivation of the catalyst under study are the deposition of Ni and V and the accumulation of heavy hydrocarbon molecules (e.g asphaltenes) in the interior of the pore structure during hydrocracking reactions [**Manuel, et al. (2000)**].

Figure (2) shows hat Ni deposited on the surface of the catalyst is higher than V. This means that V removal is higher during the operation cycles at 425°C. The data also revealed that removal of V through the reactions of asphaltenes was much faster than Ni, indicated that vanadium moieties are the most reactive .

The deactivation was reflected on the conversion of the vacuum residue as less amounts of liquid yields through the increased cycle-times.

3- Effect of cycle- length on the characterization of the catalyst:

Table (3) and Figure (3) compare the surface area, average pore diameter and pore volume of fresh and spent catalyst after 5 successive cycles. It is evident that the surface area of the catalyst suddenly decreases by about 33% after the first cycle followed by slight decrease with the cycles 2-5. The same but to a less extent is observed when the

average pore radius of the fresh catalyst and these of catalysts operating for 1-5 cycles. The most drastic decrease is observed with the total pore volume. These tremendous changes in the textural properties may explain the significant deactivation of the catalyst because coke formation was reported to bring about 10-50% of the catalyst deactivation **[Matsushita, et al. (2004); Marafi & Stanislous (1997); Marafi & Stanislous (2001);Richordson, et al. (1996) and Wivel, et al. (1991)]**. Coke deposition causes partial blocking of the pores **[Gray, (1994)]**, masking the active acidic sites **[Bagdanor & Rase (1986)]** and possibly changes the Mo/W profile.
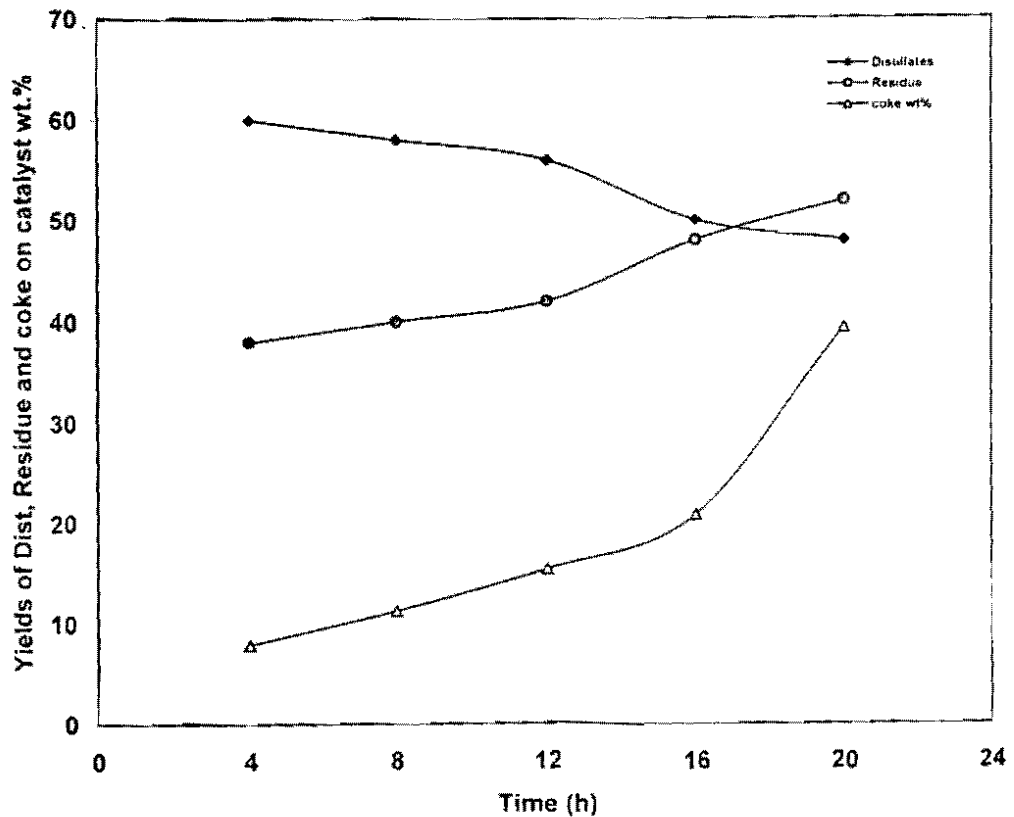

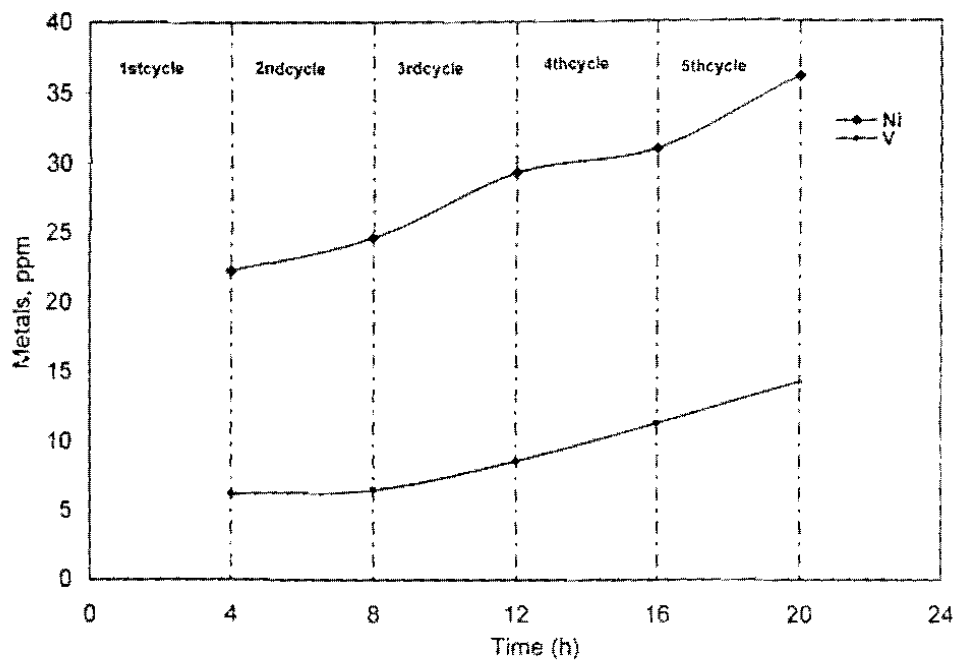Fig. (1) Effect of operation time on catalyst hydrocracking activity of vacuum heavy residue

Fig. (2) Effect of of the operatione time on catalyst metal
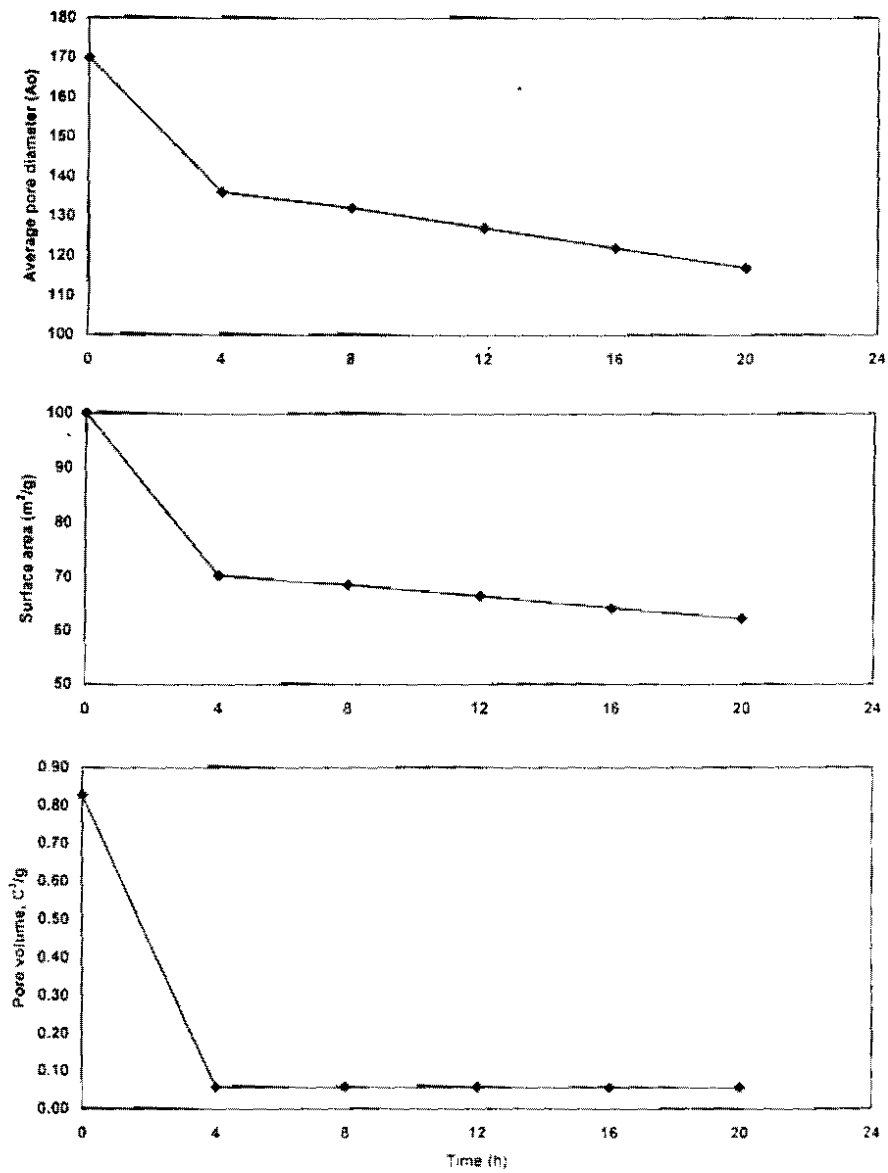deposition through hydrocaracking of vacuum heavy residue

Fig (3) Effect of operating time on the physical characteristics of the hydrocracking catalyst

Table (3): Effect of cycle-length (h) on the characteristics of
MoW- Si-Al catalyst .

	Fresh	Number of cycle-length				
		1	2	3	4	5
Surface area m2/g	104	70.30	68.6	66.03	64.20	62.26
Reduction, %		67.27	65.65	63.57	61.44	59.68
Average pore diameter A°	170	136	132	127	122	118
Reduction, %		80	77.64	74.71	71.76	69.41
Pore volume cm3/g	0.827	0.0570	0.0568	0.0566	0.0564	0.0562
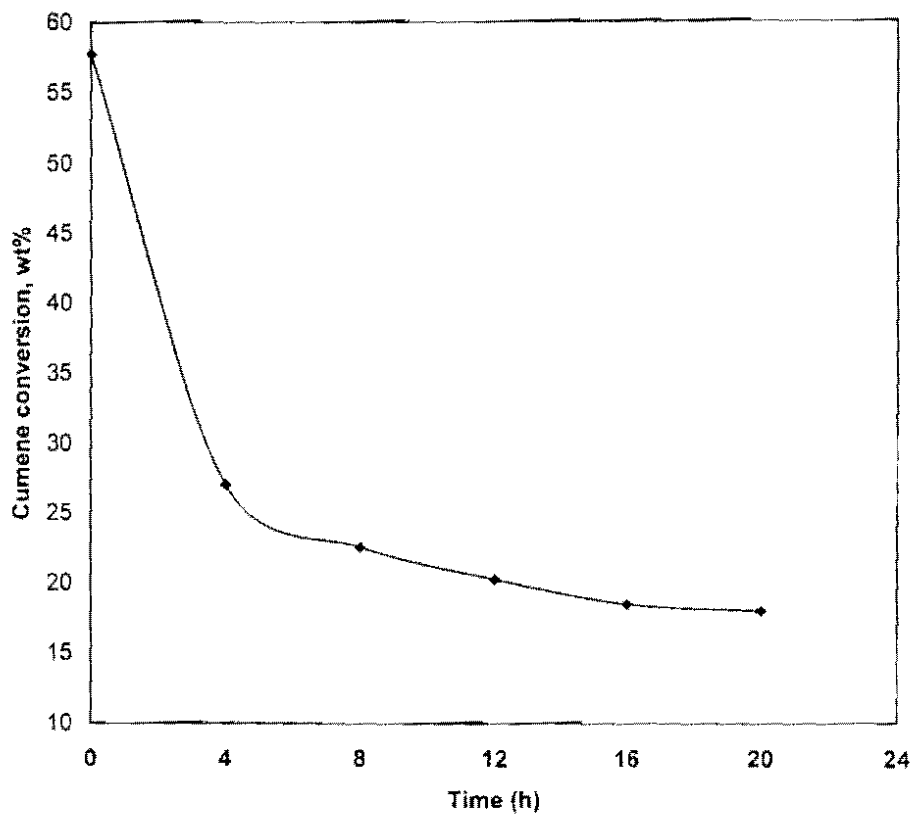
Fig. (4): Effect of operation time (h) on spent catalyst as a
function of conversion of cumene cracking using pulssing-reactor

4- Catalytic activity of spent catalysts:-

The pulsed- microreactor was used to test the catalytic activity of the fresh and used catalysts towards cumene cracking, Fig. (4) .It is shown that the catalyst looses about 53% of its activity towards cumene cracking after one cycle {4h}. For the cycles 2-5, the decrease in the activity ranges between 61-69%, respectively. It seems that coke deposition after the first cycle is responsible for the sudden decrease in the activity of the catalyst. The deactivation after the first cycle may be attributed to the deposition of Ni and V during the successive cycles with their effect attributed to poisoning of the active sites **[Gray, (1994) and Zeuthers, et al. (1995)].**

CONCLUSION

Deposition of carbonaceous materials on Mo W catalysts causes significant deactivation. The initial amount of coke deposition brings about the drastic decrease in catalyst activity {during the 1st cycle}. During cycles 2-4 lasting for 16 h more, the deposition of coke continues and causes poisoning of the active sites probably via masking of these sites to become inaccessible for reacting molecules. Heavy metal deposition {Ni and V} exhibit their deactivation effect after the 1st cycle and their effect continues with time. The deposition of coke and heavy metals causes also tremendous changes in textural properties of the catalyst and also in Mo/ W profile. These changes contribute also to the deactivation of the catalyst towards cumene cracking.

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تهميد الحفاز خلال التكسير الهيدروجينى للمقطر الثقيل المفرغ

فــى هذا البحث تم دراسة تأثير زمن التفاعل على تهميد حفاز Mo-W-Si-Al أثناء التكسـير الهيدروجيــنى للمقطــر الثقيل. كان زمن دورة التفاعل ٤ ساعات ودرجة الحرارة ٤٢٥ م . حدث ترسيب مبكر لكربون وبذلك قلت كفاءة الحفاز نتيجة هذا الترسيب بالإضافة الــى ترسيب الفلزات الثقيلة. إزداد الترسيب بزيادة إستخدام الحفاز بطول زمن دورة التفاعل وكذلــك بســبب تتابع دورات التفاعل. وقد تم تتبع تهميد الحفاز بقياس كفاءة الحفاز بعد كل دورة فى تحويل الكيومين بإستخدام تفاعل النبض الميكرونى مع جهاز كروماتوجرافيا الغاز .