KINETICS OF HYDRODESULFURIZATION CATALYST REJUVENATION PROCESS

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ABSTRACT

The present work deals with the rejuvenation of spent NiMo/Al₂O₃ hydrodesulfurization catalyst by selective leaching of the deposited metals using organic acid. Temperature in the range of 298-348 K and leaching reagent concentration (0.2-1.0 M) and time of rejuvenation were investigated in case of coked and de-coked catalyst to indicate the effect of the deposited coke in the pores of the catalyst. A Pyrex up-flow reactor of 17 mm diameter and 600 mm length (volume of the reactor 136 ml) was used.

The results indicated that the diffusion through ash layer is the controlling step especially in the temperature range of 298-323 K. At higher temperatures deviation from ash diffusion layer is noticed.

INTRODUCTION

The effect of deposited metals on hydrodesulfurization catalysts has long been recognized. The contamination with nickel, vanadium and iron leads to loss of activity, selectivity and surface area. Deactivation by metal accumulation may take form of active site poisoning, pore mouth plugging or a combination of both (1). The removal of these metal contaminates by means of a chemical technique had received considerable attention (2).

Catalyst dumping is environmentally intolerable; recovery of metals from spent catalyst is possible but the low price of recovered material makes this process unfeasible. The most economic means of catalyst treatment would therefore be the regeneration of hydrodesulfrization catalysts. The removal of deposited metals on the catalyst with the aim to recover catalyst activity is referred as rejuvenation. Organic reagent capable of forming water-soluble complexes appeared to offer a promising solvent for this industrial and environmental problem. Any regeneration process should selectively remove the contaminants while leaving the catalytically active metals intact. It has been revealed that the kinetic and mechanisms of metal leaching from spent hydrotreating catalysts have received little attention (3).

In the present work, the rejuvenation of spent NiMo/Al2O3 used in hydrode-sulfurization processes in Al-Dura Refinery was studied using different complexing agents.

Kinetic Model of the Rejuvenation Process

Spent catalysts contain a matrix of coke, which is not removed by leaching. As a result the shrinking core model should be applied in the study of the kinetic model of the rejuvenation process (4,5).

The effective diffusivity term includes both the normal or molecular diffusion (Dm) and the interphase diffusion or as known as Knudsen diffusion (DK). According to Levenspiel (6,7) the Knudsen regime is the predominate diffusion in porous catalyst. Thus the effective diffusivity term can be represented as follows:

$$D_{eff} = \frac{\xi D_K}{\tau} \qquad (1)$$

According to Carberry (4) DK is computed from the Knudsen equation:

$$D_K = 9700\, r_p \sqrt{\frac{T}{M}} \qquad (2)$$

$$r_p = \frac{2\, V_p}{S} = \frac{2\, \xi}{S\, \rho} \qquad (3)$$

Then

$$D_{eff} = 19400 \times 10^{-4}\, \frac{\xi^2}{\tau\, S\, \rho} \sqrt{\frac{T}{M}} \qquad (4)$$

Where;

ξ = the pellets porosity, τ= the tortuosity and according to Smith (5) and Satterfield (8) they summarized data from the literature and found that the tortuosity ranges from $\sqrt{2}$ to 10 and as high as 12, they recommended the use of tortuosity equals to 4.

T = absolute temperature (K).

M = molecular weight of diffusing species.

S = BET surface area of the catalyst.

ρ=pellet density

rp = pore radius (cm)

Marafi et al. (9,10) studied the regeneration of CoMo/Al2O3 spent catalyst using oxalic acid as the leaching solution. They found out that the process is pore diffusion control at 298 K. They did not mention the behavior at temperature higher than 298 K even though they worked in a temperature range of 298-348 K.

EXPERIMENTAL WORK

The Materials

1. Oxalic, tartaric and citric acids. All analar grades are purchased from Fluka.
2. Light naphtha supplied by Al-Dura Refinery.
3. Spent NiMo/Al2O3 catalyst provided by Al-Dura Refinery.

The Analysis

1. The metal content, percentage metal leached from the catalyst was evaluated by atomic absorption spectrophotometer (PYE UNICAM SP9). Analysis was done in Al-Basil Company.
2. BET surface area of the spent catalyst was measured using a Carl-Erabasorptomic series 1800 apparatus in Al-Majid Company. The surface area was measured to be 100 m2/g.
3. Pore size was determined by Quantachrom Auto Scan 60 Mercury Porosimeter. The pore size was found equal to 11.49 Å.
4. Apparent porosity was determined using the liquid impregnation method.

The Procedure

The rejuvenation procedure steps adapted in the present research could be summarized as follows:

1. The catalyst was sieved to 1.68 mm-0.71 nm (10-20 mesh) in order to clean the catalyst from dust and grounded catalyst particles for the spent catalyst is known to be brittle.
2. Residual oil was removed by thoroughly washing with naphtha in a mechanical shaker then the cleaned catalyst was dried in an oven at 393 K for 24 hours.
3. For the part when the catalyst is de-coked, the catalyst from step 2 is subjected to roasting in air at 873 K for 6 hours in order to ensure that all the coke is burned off. As for the case when the catalyst is employed without de-coking, this step is not included.
4. The acid at the required concentration was prepared and was placed in a vessel and was pumped by the dosing pump in an up-flow direction through the reactor. The acid was collected and then recirculated continuously through the catalyst bed for the required period of time.
5. Samples of the acid were taken at specified intervals to measure the amount of metals leached from the catalyst. The total time of the run is 16 hours and samples were taken at fixed periods according to the conditions of each run.
6. The temperature range is 298-349 K and runs were performed at 298, 308, 323, 338 and 348 K. The organic acid concentration ranged between 0.2-1.0 M (0.2, 0.4, 0.6, 0.8 and 1.0).

The Reactor

A Pyrex up-flow reactor of 17 mm diameter and 600 mm length (volume of the reactor 136 ml) was used. The reactor consisted of three sections, these sections are:

1. The preheating zone was packed with small cylindrical Pyrex glass to preheat the organic acid up to the desired temperature of rejuvenation. The length of this section is approximately 25 cm, this length was presumed to be sufficient for heat transfer to be achieved.

2. The reaction zone contains 25 ml of the spent catalyst; the length is approximately 10 cm.
3. The last section is filled with Pyrex packing to ensure that no catalyst particles may be carried with the flowing rejuvenating acid.

The reactor was heated with a heating tape; a voltage regulator controlled the heating and the digital thermometer mounted vertically at the reaction zone measured the temperature. Figure (1) shows a schematic diagram of the experimental rig.

RESULTS AND DISCUSSION

The rejuvenation process was carried out using a diluted aqueous solution of organic acid as a complexing agent. Oxalic acid was noticed to be more effective in the rejuvenation of spent NiMo/Al2O3 hydrodesulfurization catalyst when compared with citric and tartaric acid. Although the three acids succeeded in leaching the metals from the spent catalyst as shown in table (1).

Table (1) Surface Area, Porosity and Percentage of Metal Removed from Spent $NiMo/Al_2O_3$ using ifferent Types of Leaching Acids (Acid Concentration = 0.6 M and Temperature = 323 K)

Acid Used	Surface Area (m^2/g)	Porosity	Percentage of Metal Removed		
			Ni	V	Fe
Oxalic	151.5	0.47	5.76	14.20	4.63
Citric	148	0.455	5.20	12.5	4.12
Tartaric	142	0.425	4.93	10.00	3.8

Figures (2 and 3) show results of plotting equation (5).

$$\frac{t}{\tau}=X_B+(1-X_B)\ln(1-X_B) \qquad (5)$$

where

$\tau$is the time needed for complete conversion.

$$\tau=\frac{\rho_B R^2}{4 b D_{eff} C_{A_f}} \qquad (6)$$

The rejuvenation data are applied for both cases of coked and de-coked catalyst as a function of temperature at constant acid concentration (2). Figures (4 and 5) show temperature effect on porosity and surface area of oxalic acid concentration of 0.6 M. It is shown that when the temperature is increased the porosity and surface area consequently increased. The increase in porosity and surface area is more pronounced in case of de-cocked catalyst. This could be due to the fact that metal containing impurities are deposited in the pores of the catalyst pellets and within the coke matrix. Thus on removing the coke prior to leaching process, part of the resistance to leaching process might be reduced and consequently mass transfer is enhanced. Statistical analysis results are given in table (2).

Table (2) Statistical Analysis of the Diffusion through Ash Layer at Different Rejuvenation Temperature and Oxalic Acid Concentration of 0.6 M for Spent Catalyst in Case of Coked and De-coked

Temperature (K)	Correlation Coefficient	
	Coked	De-coked
298	0.950	0.926
308	0.936	0.902
323	0.890	0.845
338	0.885	0.84
348	0.897	0.85

It is seen that the ash-diffusion control (diffusion through pores) represents the mechanism of the rejuvenation process especially for the case of low temperature namely in the range of 298-323 K. As the temperature increases, deviation from the ash-diffusion control is noticed and this might be attributed to the increase of the rate of mass transfer with the increase in temperature indicating that other types of mechanism might be interfering.

Furthermore, it seen that in case of coked catalyst the diffusion through ash layer mechanism is much more prominent. This might be attributed to the existence of a coke matrix deposited in the pores of the catalyst causing resistance to mass transfer. While in case of de-coked catalyst, the removal of most of the carbon might cause an enhancement of mass transfer through the pores as seen in table (2) in comparing between the correlation coefficient for both cases.

Results of Marafi et al. (9) advocated our results concerning the controlling mechanism, but they only concentrated their study on 298 K and for coked catalyst and did not extended their work for higher temperatures.

CONCLUSIONS

1. Oxalic acid is respected to be more efficient in the rejuvenation of spent NiMo/Al2O3 hydrodesulfurization catalyst when compared with citric and tartaric acid. The order of efficiency is oxalic acid > citric acid > tartaric acid.
2. The controlling mechanism of the rejuvenation process is ash diffusion control (diffusion through pores). Deviation from this mechanism was noticed as the temperature increased above 50 °C and was attributed to the increase in mass transfer rate with temperature.

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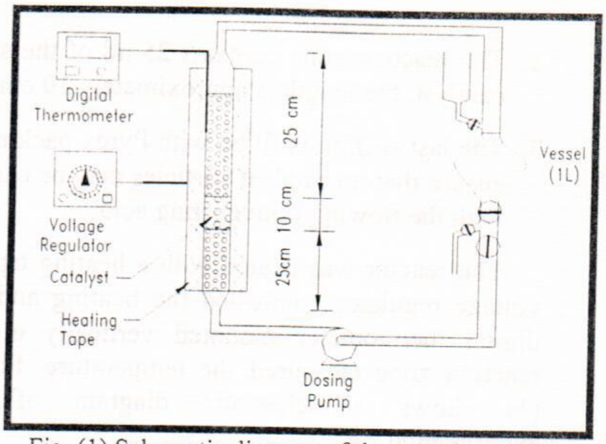

Fig. (1) Schematic diagram of the experimental rig

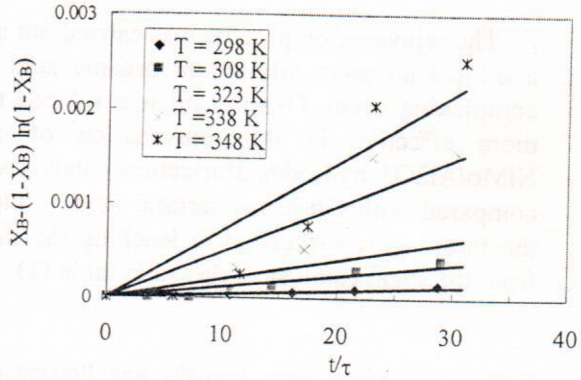

Fig. (2) Diffusion through the ash layer for coked catalyst

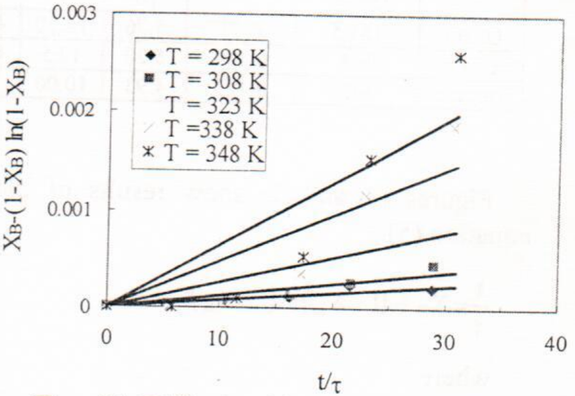

Fig. (3) Diffusion through the ash layer for de-coked catalyst