Effect of Leaching Conditions on Spent Catalyst Metal Recovery

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ABSTRACT

Recovery of transition metals (vanadium, molybdenum, tungsten, nickel, etc) from spent petroleum refining catalysts is an important industrial problem because of the need for making new catalyst and disposal of enormous amounts of deactivated catalysts. According to reported data, many steps processing involving various oxidants or reluctant in basic or acidic media and with different thermal conditions have been developed.

Waste hydrotrating catalyst (NiMo) which have been used in re-reing of waste lube oil at Alexandria Petroleum Company (after one year lifetime) was used in this study.

Metal recovery were leached from the spent catalyst by using solution of (4%oxalic acid + 5% H2O2) used as a leaching solvent. The present work deals with the effect leaching of temperature (25° - 100°C) and time (50-350min) on total and selective metal in order to re-use these metals in different applications.

Total metal recovery was increased sharply from 14.95 wt% at 25°C to 27.7 wt% at 75°C above which the increase became slowly. And also total metal recovery was increased from 13.7 wt% at 50 min to 17 wt% at 150min above which the increase become slowly.

The results indicated that in order to keep the active metals of the spent catalyst referred lower temperature and lower time.

In order to other uses such as reuse as additive in cartain applications, reffered higher temperature and higher time.

INTRODUCTION

The petroleum refining industry makes extensive use of catalysts for the hydrodesulfrization of the various oil fractions. Catalysts for hydrodesulfrization

contein critical metals, such as, Mo, Co and Ni generally supported by alumina or silica aluminates. The life time of a hydrodesulfrization catalyst, after several intermediate regeneration options, is from 3 to 6 years (1). During hydro desulfrization the catalysts are deactivated by compounds of S, C, V, Fe, Ni, Si and traces of a As and p (2).

Recovery of transition metals vanadium, molybdenum, tangesting nickel, etc) from spent petroleum refining catalysts is an important industrial problem because of the need for making new catalyst and disposal of enormous amounts of deactivated catalysts. According to reported data (3-6) , many . step processing involving various oxidants or reductant in basic or acidic media and with different thermal conditions have been developed. it is known that each refining company uses catalysts having various composition depending on many factors. Therefore existing recovery methods should be adjusted to the industrial conditions and problems in this work a possibility for recovery the molybdenum, Nickel, alumina and other metals from waste lube oil spent petroleum. re refining catalyst under different extraction condition temperature and was time studied using oxalic acid as a solvent and H202as oxidizing agent.

EXPERIMENTAL:-

1.1 spent catalyst kindly provided from the re-refining waste lube oil hydrotreating unit of Alexandria petroleum company. Table (1) shows the characteristics of the fresh (sud-chim) and spent catalyst (one year life time)

1.2. spent catalyst treatment

The catalyst was in the form of extrodates and contained lube oils, sulfur, carbon, metal deposits in addition to the active catalyst metals.

The catalyst contaminates such as residual lube oil, sulfur and coke were removed as describe elsewhere in situe (7).

1.3 Leaching treatment

4% oxalic acid solution with addition of 5% H202 as oxidized agent was used for the leaching experiments. 250 ml of this solution was added to 25g of the pretreated

decoked spent catalyst on a 500ml pyrex conical Flask equiped with a reflux condenser at the following conditions:-

Leaching Temp. : 25° - 50 - 75 - 100°C

Stirring time: 50° - 100 -120 -150 - 200 - 250 - 300 - 350

The selection was stirred duing the experimental comnditions and adjusted the PH to1 At the end of different leaching conditions the catalyst was cooled to room temperature, and then. Filtered. The Filtrate which having the metal recovery was analyzed by atomic absorption spectro photometer (Prkin Elmer 80) and silica by gravimetric method.

The activity test of the catalyst was experimentally done using GLC-pulsed reactor. Where the reactor tube was connected to the injection port of the tube was connected to the injection port of the GLC-unit, containg 0.2g of the .tested catalyst sample and using heptene-2 as the reactant feed

RESULT AND DISCUSSION

1- Effect of temperature on metal recovery

The effect of temperature on total metal recovery was studied by performing experiments at, 25°, 50, 75 and 100°C: as leaching temperatures (table 2 and fig. 1). The data indicated hat the leaching temperatures has influenced the metal recovery. It means that the total metal recovery increases sharply from 14.95wt % at 25 to 27.70 wt % at 75° C above which, the increases become slowly to reach 29.18 wt% at 100°C. These results are attributed to the dissolutions of metals which was affected by temperatures in the range up to 80° and facilitate the metal separation. The rate of metals recovery was affected too by increasing temperature and noticed to be decreased due to the effects of raising reaction temp which use continues evaporation of the solutions and producing as protective oxide layer of these metals (8) preventing their dissolution at higher temperatures .

Table (3) and Fig. (2) represent the behavior of the selection metals leaching during increasing temperature from 25°C to 100°C and indicated that; (Ni , AL and Si) were increased by increases temperature. (Mo, P and other metals) were decreased by

increasing temperature, therefor, when reuse of the treated spent catalyst, it recommended to proceed the Job at lower temperature, in order to keep the active metals in a new catalytic form for industrial applications.

Hydrocarbon conversion application:

The solid residue of the spent catalyst and oxidize oxalic acid solution at 75oC was selected for its elements of interest. The chemical analysis gave the composition of Mo-Ni catalyst: 2.38% Mo, 2.3% Ni and 26.82% Al beside the other components, such as 11.29% Si and 0.42% P. Experimental run was conducted on heptene-2 olefin as a model hydrocarbon using the selected treated catalyst in order to determine the reaction activity towards olefin conversion in a pulse-technique GC-tool. The results are indicated in (Fig.5). The data indicate that, in comparing with the fresh catalyst sample, under the experimental conditions, the olefin conversion and isomerization activities are greatly affect by reaction temperature. The total conversion was observed to be at maximum (86%) at lower temperature and decreased as temperature increased. On the other hand, total isomerization activity was increased with increasing temperature, i.e as the raising in reaction temperatures, the formed hydrocarbon; n-heptane, was cracked to lower molecules, which in turn, subjected to in isomerize via the active carboneum ions. The resulted data reveal that the selected treated spent catalyst can be used for hydrogenation reaction for hexanes or heptanes treatments at low temperature.

Other uses of the were performed by extracting most of the spent catalysts metals at higher temperature for reuse as additive in certain applications such as, cement mortar, glass ceramic (9,10)

2- Effect of time on metals recovery

Table 4 and fig 3 illustrate the significant effect of time on the total metal recovery which increased by increasing leaching time prolonging contact of leaching solutions on the spent catalyst under study shows a noticeable fast increase of dissolution reaction of its metals content, i.e. from 50 to 150 min, followed by a steady increase through the periods 150-350min. The fast increase was observed to be 13.7 to

17.0 wt% (nearly 120 folds). A steady state was reached at higher time rather than 150min, i.e from 17.33 to 18.18wt% at 200 and 350min respectively (~ 105 folds). The obtained data were attributed to the effective of H_2O_3 added to the leaching acid, and enhanced the leaching to form metal ions rapidly dissolute the products from their sulfide forms. Therefore, the higher oxidized metal forms were complexed by the oxalate ion and / kept in solution. The leaching rate will be dictated by the concentration of the oxalate agent and the time of leaching (Fig 3). It means that the initial rate of leaching is nearly rapid till 150 min, and after that a steady state was observed due to the used up of the reagents with time (11).

In case of the selectivity of the leaching reagents for the individual metals, Figure (4) indicated The leaching agents have very lower activities towards most of the metals except Ni, which shows a remarkable extraction activity with increasing time and a maximum efficiency was obtained at 300min. Therefore, the reaction system reveals that reaction of leaching reagent, containing oxidizing agent would be more effective in converting the low-valent nickel metal sulfides to favorable higher oxidation states for extraction.

CONCLUSIONS

A comparative assessment of different modes of metal leaching of oxidized oxalic acid on the extraction of metals from the hydrotreating spent catalyst was studied in order to reuse its metals. The results revealed that either temperature or time of leaching have enhancing characters on the leaching activity of metals content. According to environmental considerations it is very useful to reuse the solid spent catalysts to produce a salable metal products such as nickel salts, and alumina in different industrial applications.

Table (1):Characteristics of Fresh and the Waste Lube Oil Spent Catalyst as Metal%

Chemical composition, wt%	Fresh	Spent
Mo	15.03	9.79
Ni	3.57	2.68
Al	34.74	32.81
Si	---	11.55
P	---	3.12
(Zn, Fe, Mg, Ca, K, Na)	0.550	0.713

Table (2) Effect of leaching temperature on metal Recovery at constant pH and stirring time

Metals / Temp.	Metals on spent catalyst	25°C	50°C	75°C	100°C
Metals content, wt%					
Ni	2.68	0.04	0.29	0.38	0.63
Mo	9.79	5.15	7.22	7.41	7.35
Al	32.81	2.06	4.97	5.99	6.66
Si	11.55	0.07	0.24	0.26	0.36
P	3.12	1.70	2.67	2.70	2.61
Other metals (Z n,Fe, Mg, Ca, K, Na)	0.71	0.05	0.06	0.06	0.08
Total metals, wt%	60.66	9.07	15.45	16.8	17.7
% Metals recovered	0	14.95	25.47	27.70	29.18
Rate of Total metal recovery %		70.37	8.76	5.34	

Table (3) Effect of leaching temperature on metal Recovery at constant pH and stirring time

Metals / Temp.	Metals on spent catalyst	25°C	50°C	75°C	100°C
Distribution					
Ni	4.42	0.44	1.88	2.26	3.56
Mo	16.14	56.78	46.73	44.11	41.53
Al	54.09	22.71	32.17	35.65	37.63
Si	19.06	0.77	1.55	1.55	2.15
P	5.14	18.74	17.29	16.07	14.75
Other metals (Zn, Fe Mg, Ca, K,Na)	1.17	0.55	0.39	0.36	0.33

Table (4) Effect of leaching time on metal Recovery at constant pH and temperature, 25°C

Metals / Time.	Metals on spent catalyst	50	100	120	150	200	250	300	350
Metals content wt%									
Ni	2.68	0.02	0.03	0.04	0.06	0.11	0.14	0 .14	0.13
Mo	9.79	4.95	4.95	5.15	5.81	5 .89	5.83	5.71	5.63
Al	32.81	1.78	1.89	2.06	2.41	2.54	2. 61	2 .80	2 .88
Si	11.55	0.07	0.06	0.07	0.08	0.086	0.09	0.097	0.1
P	3.12	1.44	1.51	1.7	1.9	1.84	1.98	2.09	2.25
Other metals (Zn, Fe, Mg, K, Ca Na)	0.71	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04
Total metals wt%	60.66	8.31	8.49	9.07	10.31	10.51	10.69	10.88	11.03
%Metal recovery	0	13.7	14	14.95	17	17.33	17.62	17.94	18.18
Rate of total metal recovery		2.19	6.64	11.42	1.88	1.79	1.76	1.33	

Table (5) Effect of leaching time on metal Recovery Distribution at constant pH and temperature,25°C

Metals / Time.	Metals on spent catalyst	50	100	120	150	200	250	300	350
Distribution %									
Ni	4.42	0.24	0.3	0.44	0.58	1.05	1.31	1.3	1.18
Mo	16.14	59.22	58.18	56.78	56.35	56.04	54.54	52.52	51.04
Al	54.09	21.42	22.26	22.71	23.38	24.21	24.44	25.74	26.11
Si	19.06	0.71	0.72	0.77	0.8	0.82	0.87	0.89	0.91
P	5.14	17.33	17.79	18.74	18.43	17.51	18.52	19.19	20.44
Other metals (Zn, Fe, Mg, Ca, k, Na)	1.17	0.60	0.59	0.55	0.48	0.38	0.37	0.36	0.36

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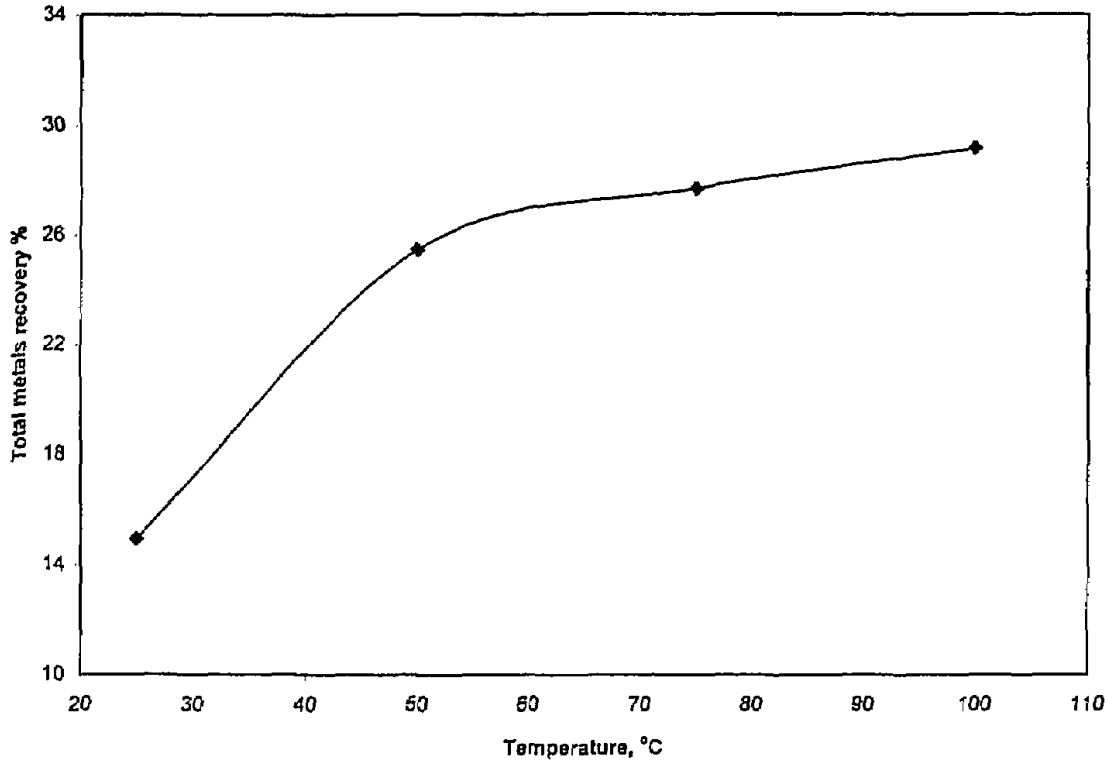

Fig. (1): Effect of Leaching temperature on total metal Recovery

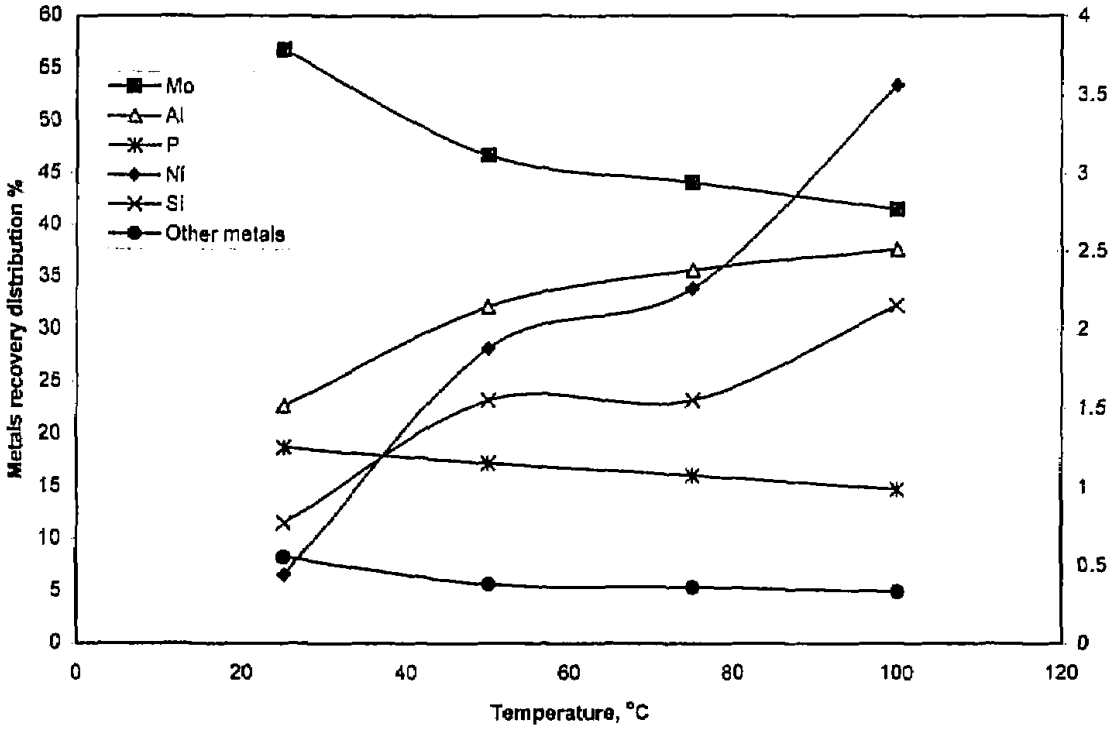

Fig. (2): Effect of Leaching temperature on Metal recovery Distribution

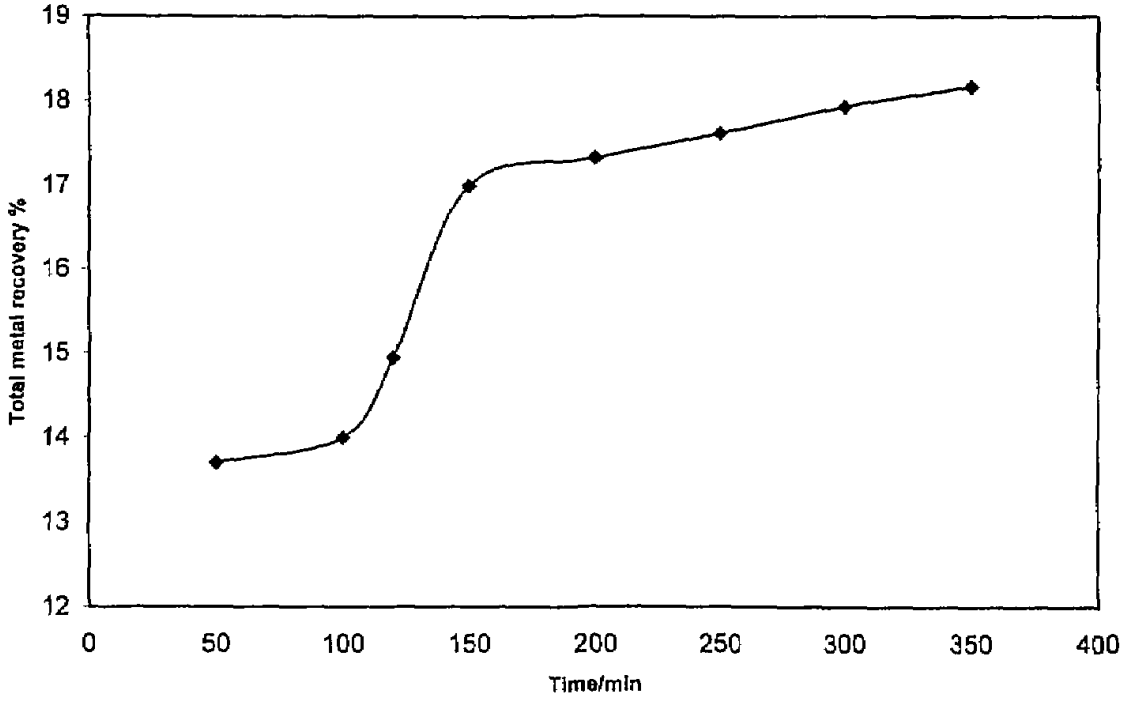

Fig. (3): Effect of leaching time on total metal recovery

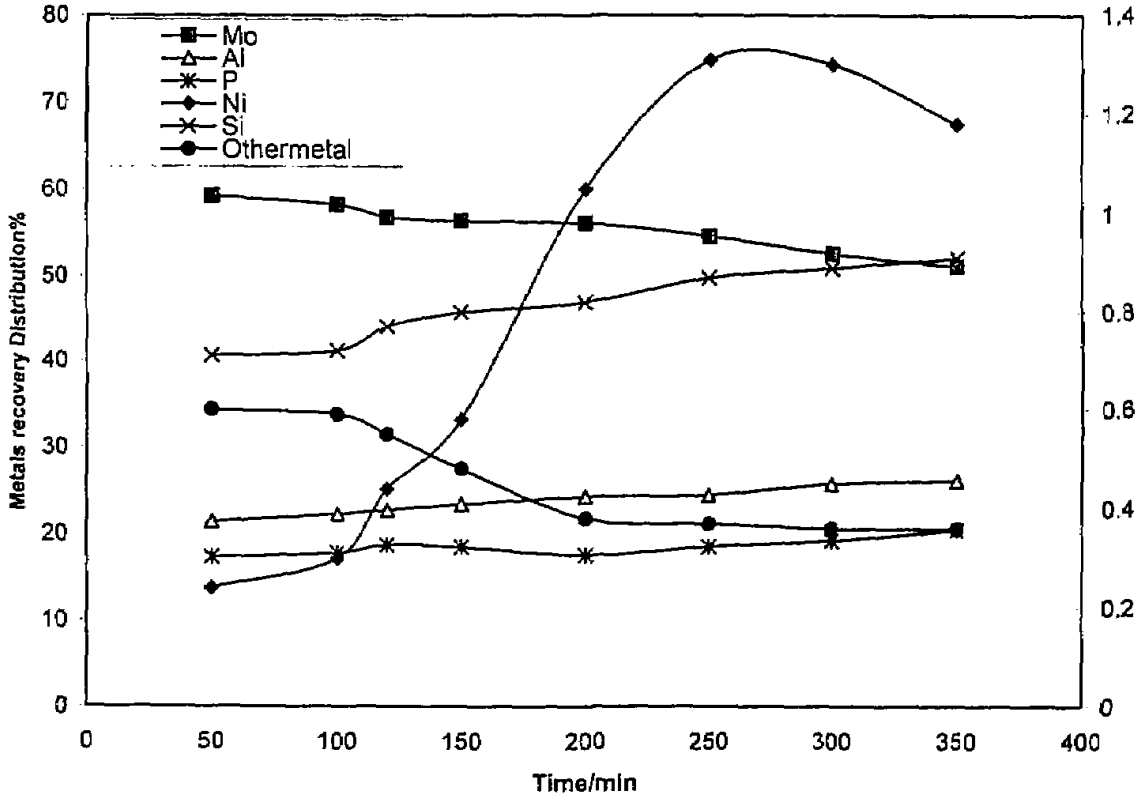

Fig (4): Effect of leaching Time on metal recovery Distribution

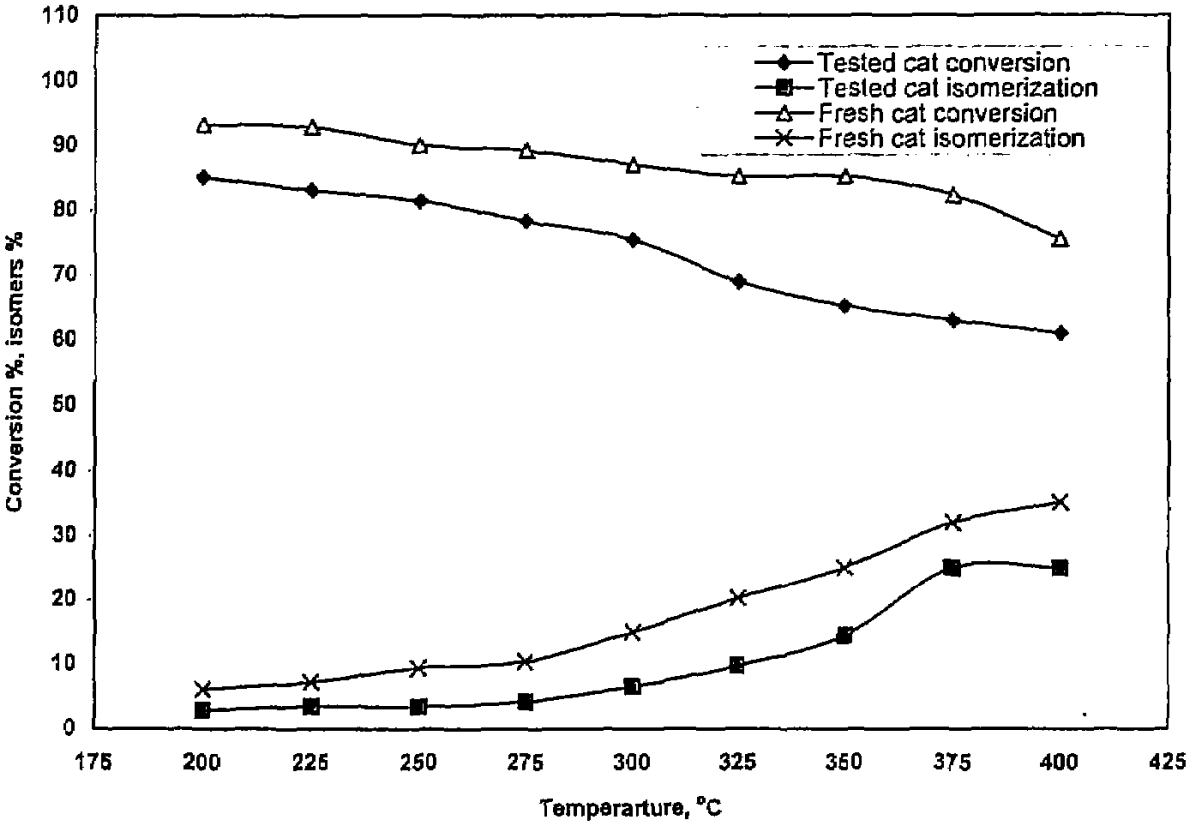

Fig. (5) Activity of the leached catalyst for heptene 2 hydrocarbon conversion of treated catalyst by 4% oxadic acid at 75°C-2h