ACTIVE ALUMINA EXTRACTION FROM IRAQI BAUXITE FOR CATALYST'S SUPPORT

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ABSTRACT

The bauxite produced from Al-Gaara Quarry in Al-Enbar containing 60.65% Al_2O_3 was used as raw material for support preparation. Bauxite had been mixed with calcium carbonate in different ratios. The mixture was burned at temperature range 1350 oC, and the products were crushed and ground. The powders treated with sodium carbonate solution using 9% concentrations and different temperatures for fifteen minutes. The produced aluminate solution reacted with 3% concentrations of calcium hydroxide at 98 oC for 30 minutes, then the filtrate was carbonated with purified CO_2 gas at 70 oC for different times. Alumina was precipitated as hydrate, then washed with water, dried at 110 oC, and calcined at 550 oC. The produced γ-Al_2O_3 was identified by X-ray.

The carriers were prepared by mixing 100 gm $Al(OH)_3$, 2.5% bauxite as binder and adding 22 gm of distilled water then aged for 24 hours. The resulted pastes were formulated by extruder. The extrudates (diameter 3 mm and length 8 mm) were dried at 110 oC for 2 hours, and calcined at 550 oC for 6 hours. Co-Mo/catalysts was prepared using prepared supports by impregnation method at specified condition. The gas oil was hydrodesulfurized using presulfide prepared Co-Mo/γ-Al_2O_3 catalysts at specified operating conditions in laboratory high pressure unit.

The comparison between the prepared and industrial catalyst show that the sulfur removal from gas oil during HDS (hydrodesulfurization) process with prepared catalyst from Gaara bauxite was higher at all operating conditions than industrial catalyst (HT-500R). The rate constants, activation energy, enthalpy and entropy were also estimated for HDS using prepared Co-Mo/γ-Al_2O_3 catalyst.

The bauxite produced from Al-Gaara Quarry in Al-Enbar containing 60.65% Al_2O_3 was used as raw material for support preparation. Bauxite had been mixed with calcium carbonate in different ratios. The mixture was burned at temperature range 1350 oC, and the products were crushed and ground. The powders treated with sodium carbonate solution using 9% concentrations and different temperatures for fifteen minutes. The produced aluminate solution reacted with 3% concentrations of calcium hydroxide at 98 oC for 30 minutes, then the filtrate was carbonated with purified CO_2 gas at 70 oC for different times. Alumina was precipitated as hydrate, then washed with water, dried at 110 oC, and calcined at 550 oC. The produced γ-Al_2O_3 was identified by X-ray.

INTRODUCTION

The major portion of alumina used in the world is made from bauxite with the Bayer process. Nepheline-syenite used as raw material for alumina production in Russia. In this process large quantities of cement by product was produced(1).

Yearly, large quantities of alumina are produced for the manufactured of metallic aluminum, abrasives, chemicals, refractories and ceramic fibers(2). The basic properties of the catalyst components are, the main determinant, but texture and stability can be influenced strongly by choosing appropriate method for preparation(3).

In this work, Gaara bauxite was studied for alumina extraction. Alumina extracted from bauxite was used for hydride-sulfurization catalyst preparation by impregnation process. Finally, the hydrodesulfurization of gas oil process carried out in laboratory high pressure unit under Co-Mo-catalyst prepared from bauxite at different operating conditions .

EXPERIMENTAL WORK

Materials

Bauxite

The bauxite produced by Al-Gaara Quarry in Al-Enbar containing 60.65% Al2O3 was used.

Limestone (Calcium Carbonate)

The calcium carbonate produced by Al-Kilo 160 in Al-Enbar containing 54.3 wt.% CaO was mixed with bauxite.

Sodium Carbonate

Sodium carbonate was supplied from BDH Chemical Limited Poole England with purity 99.98%.

Calcium Hydroxide

Calcium hydroxide was supplied from BDH Chemical Limited Poole England with purity 98.92%.

Straight-Run-Gas Oil

Straight-run-gas oil with sulfur content of 1.0% supplied from Daura-Refinery was used as feedstock for HDS process using prepared catalysts. The properties of gas oil are given in Table (1).

Table 1 Properties of straight run gas oil supplied from Daura refinery

Tests	*Value*
Specific gravity @ 15.6°C/15.6°C	0.73
Sulfur content, wt%	1.00
Pour point, °C	-10
Flash point, °C	66
ASTM-distillation, 20% distilled, °C	340

Alumina Production

Fig. (1) shows the block diagram of alumina production used in this work. Bauxite and limestone are ground, and sieved to obtain fine particle size, because large particle size will decrease the alumina extraction efficiency (4).

Bauxite particle and limestone with dimension of less than 45 μm had been mixed (1:3), then each mixture was burned in electrical furnace at temperature 1350 °C for six hours. Di-calcium silicate (C2S), calcium aluminates 12CaO.7Al2O3 (C12A7), and CaO.Al2O3 (CA) are formed (4-8).

After sintering (burning), the mixtures were crushed to fine powder (less than 37μm). Alumina is extracted from the disintegrated powder by extraction with 9% Na2CO3 solution at different temperatures ranging from 90-150 °C for fifteen minutes. Sodium carbonate treatment was repeated three times. The calcium aluminates are converted to soluble sodium aluminates as shown from the following reaction

$$CaO.Al_2O_3 + NaCO_3 \rightarrow 2NaAlO_2 + CaCO_3 \qquad (1)$$

$$12CaO.7Al_2O_3 + 12Na_2CO_3 + 5H_2O \rightarrow 14NaAlO_2 + 12CaCO_3 + 10NaOH \qquad (2)$$

Sodium aluminate was detected by sodium hydroxide solution. The insoluble which contains C2S and CaCO3 are removed by filtration.

Desilication of aluminum-rich-solution is affected by treatment with 3% calcium hydroxide at 98 °C and atmospheric pressure for thirty minutes. Desilication process was repeated three times. The desilication reaction is

$$2Na_2SiO_2 + 2NaAlO_2 + Ca(OH)_2 + 2H_2O \rightarrow CaO.Al_2O_3.2SiO_2 + 6NaOH \qquad (3)$$

The filtrate (aluminates solution) is then carbonated with CO2 gas at 70 °C for different times ranging from 30-180 min. Aluminum is precipitated as hydrate, as shown from the following reaction:

$$2Na_2AlO_2 + CO_2 + 3H_2O \rightarrow Al_2O_3.3H_2O + Na_2CO_3 \qquad (4)$$

Alumina is then washed with water for removal of sodium salt, dried at 110 °C, then calcined at 550 °C in presence of air for 6 hours. The produced γ-Al2O3 was identified by x-ray.

Catalyst Preparation

The carrier was prepared by adding 22 gm of distilled water to 100 gm of aluminum hydroxide powder of particles less than 53 μ . Then 2.5 wt.% kaolin was added for mechanical strength improvement of the catalyst. The addition of water and bauxite was carried out slowly with continuous mixing in order to achieve a homogeneous mixture. During bauxite addition at 45 °C, the solution gradually formed homogeneous paste. The paste was left for 24 hours then extruded to give a uniform extrudates

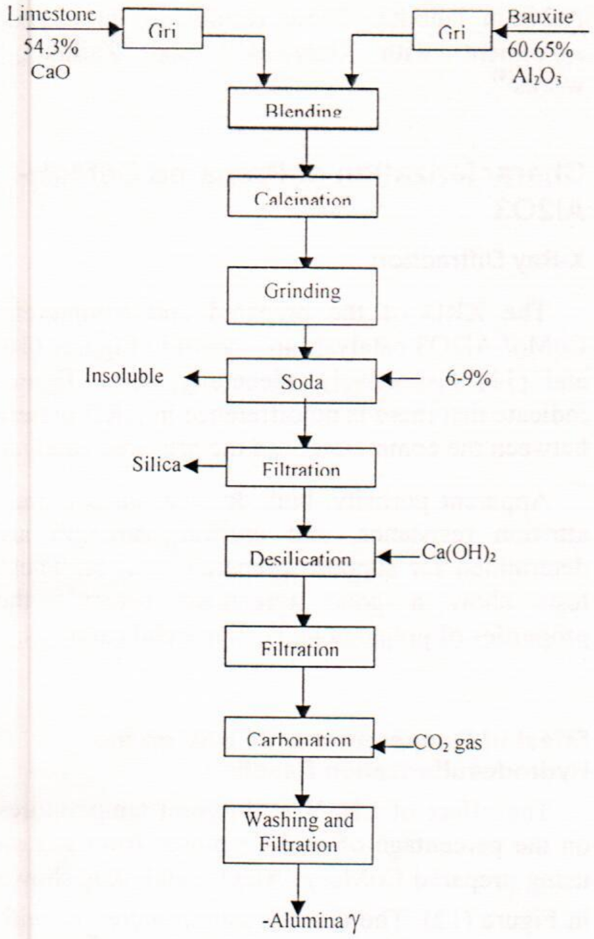

Fig. (1) Block Diagram for Alumina Production

(diameter 3 mm) which is cut into equal similar parts with length of 8 mm. These extrudates were left at room temperature for 24 hours, dried at 110 °C for 2 hours and then calcined at 550 °C for 6 hours, and finally put in dissicator.

Table 2 The chemical composition of carrier prepared from bauxite.

Al_2O_3	97.98
SiO_2	1.53
Fe_2O_3	0.19
MgO	0.1
CaO	0.09
TiO_2	0.07
Na_2O	0.04
Total	100.00

Co-Mo/γ-Al2O3 catalyst was prepared by using extrudate produced from bauxite by impregnation method.

Evacuation is operated to remove the air from the pores of the carrier. The impregnation solution is prepared by dissolving 17.6 gm of ammonium molybdate (purity 98%) in 40 ml of deionized water, then 6.8 gm of boric acid (purity 97%) dissolved in little quantity of deionized water, finally ammonium molybdate solution mixed with boric acid solution. The impregnation process was accompanied with shaking for four hours at fixed temperature of 70 °C. The impregnation alumina was dried at 110 °C overnight with air. The dried impregnated alumina is calcined at 550 °C for 6 hours under atmospheric air and placed in dissicator.

The cobalt was added by impregnation of MoO3/γ-Al2O3 using the same procedure used for molybdenum impregnation, except that the impregnation solution was prepared by dissolving 11.1 gm cobalt nitrate (purity 97.12%) in 30 ml of deionized water.

Hydrodesulfurization Experiments HDS Unit

The hydrodesulfurization experiments were performed in a laboratory continuous high-pressure unit.

Hydrodesulfurization Operating Conditions

Hydrodesulfurization of gas oil was carried out using sulfided Co-Mo/γ-Al2O3 catalyst from Gaara bauxite. The temperature range varied from 573 to 633oC with liquid hourly space velocity ranging from 1 to 4 hr-1. The pressure and hydrogen feed ratio was kept constant at 25 bar and 200 l/l, respectively.

Test Method

Apparent porosity, pH measurement, bulk density, surface area, crushing strength and attrition resistance were determined using procedure edited by Alfred (9) and Johs et al. (10) respectively.

X-ray diffraction (XRD) is mostly used for bulk structure analysis. Peak identification were made on the basis of d-spacing f typical compounds are given in the ASTM powder difference file. The x-ray diffraction of catalyst and it's carrier (γ-alumina) were carried out using x-ray diffractometer (wave length 1.524 A°, 40 kV and 20 mA).

Finally, sulfur content of straight-run-gas oil and the hydrodesulfurized products obtained by the quartz-tube method (IP 63/55)$^{(11)}$.

RESULTS AND DISCUSSION

Support and Catalyst Preparation

Figures (2) and (3) show the effect of carbon dioxide gas flow rate on the percentage extraction and yield of Al(OH)$_3$, respectively.

The increasing in CO2 gas flow rate increases the extracted Al(OH)3 from bauxite, yield of Al(OH)3 based on Al2O3 in bauxite and yield based on Bauxite. These results are in agreement with Grzymek$^{(5)}$ and Zaifakonik works$^{(4)}$. The selected flow rate of CO2 gas was 60 cm3/min for 1000 cm^3 of sodium aluminates solution. The flow rate was slightly more than that needing for the following precipitation reaction:

Higher flow rates have a little effect on Al(OH)3 extraction and the yields. Figures (4) and (5) show the effect of carbonation time in the range 30-240 min. on the percentage extraction of Al(OH)$_3$, yield based on Al2O$_3$ on yield based on bauxite.

These figures show that the increasing in carbonation time increases the alumina hydrate extraction and the yields. But at the same time, it could be noticed that the increasing in carbonation times increases the particle size of Al(OH)$_3$, as explained by Tschamper$^{(12)}$.

The increasing in particle size of Al(OH)$_3$ causes a decrease in surface area of prepared carrier (γ-Al$_2$O$_3$) as shown from Figure (6) and increase in pH of precipitated Al(OH)$_3$ as shown in Fig. (7).

From the above discussion, it's possible to consider that the optimum carbonation time is two hours.

The effect of sodium carbonate treatment was studied at different temperatures ranging from 90-150 °C. Figures (8) and (9) show that the percentage of Al(OH)$_3$ extraction and the yield increase with temperature increasing.

The addition of Na$_2$CO$_3$ to the sintered mixtures increases both the rate of the reaction and the formation of the soluble alumina compounds. It is possible to consider that the optimum sodium carbonate treatment temperature is 130 °C, because higher temperature gives slightly effect on Al(OH)$_3$ extraction, yields of Al(OH)3 based on bauxite, and yields based on Al2O3in bauxite. These results are in a good agreement with Grzymek$^{(5)}$ and Zaifakonik works$^{(4)}$.

Characterization of Prepared CoMo/γ-Al2O3

X-Ray Diffraction

The XRD of the prepared and commercial CoMo/-Al2O3 catalysts are shown in Figures (10) and (11) respectively. Generally, these figures indicate that there is no difference in XRD pattern between the commercial and the prepared catalyst.

Apparent porosity, bulk density, surface area, attrition resistance, and crushing strength are determined for support, prepared catalyst. These tests show a good agreement between the properties of prepared and commercial catalysts.

Effect of Temperature and LHSV on the Hydrodesulfurization Reaction

The effect of LHSV at different temperatures on the percentage of sulfur removal from gas oil using prepared CoMo/γ-Al2O$_3$ catalyst is shown in Figure (12). The desulfurization increases with increasing temperature and decreasing LHSV. These results are in agreement with other studies on the hydrodesulfurization of several gas oil$^{(13-17)}$.

Figure (13) show the effect of LHSV on sulfur removal from gas oil at different temperatures using industrial catalyst HT-500R(13). The comparison between Figures (12) and (13) show that the sulfur removal from gas oil during the HDS process using prepared catalyst was higher than industrial catalyst HT-500R. This may be due the higher surface area of the prepared catalyst compared with industrial catalyst HT-500R (146.5 m^2/gm).

Kinetic of Hydrodesulfurization Process

The results of Fig (14) show that the hydrodesulfurization data have a clear deviation from ideal first order kinetic model. This is in agreement with Scott and Bridge work $^{(18)}$.

Figure (15) show a plot of log (ln Cs in/Cs out) vs. log (1/LHSV) which yields straight lines with slopes equal to $(1-\beta)$. According to the hold up model of Henry and Gilbert (19) the value of β ranges from 0.46-0.63 were obtained.. The value of β seems to depend on the reaction conditions (i. e., temperature, pressure, and LHSV) and the nature of the reaction (20, 19 and 21).

Second order kinetic model used to fit the data obtained. Plotting $\left(\frac{1}{C_{s\ out}}-\frac{1}{C_{s\ in}}\right) vs. \left(\frac{1}{LHSV}\right)$ at different temperatures gives straight lines with slopes equal to the rate constant as shown in Figure (16). These results are in agreement with that obtained by A. H. Mohammed, and others(13) and Scott(18).

Thermodynamics of the Hydrodesulfurization Process

The activation energy measures the amount of energy, which the reactants must have before they can overcome the barrier between them and the product state. The activation energy for the hydride-sulfurization reaction was calculated using the Arrhenius equation that satisfies the relationship between the rate constant and the reaction temperature $^{(22)}$.

$$k = A_o \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

A plot of ln k vs. (1/T) as shown in Figure (17) gave a straight line with a slope equal to –Ea/R from which the activation energy for HDS process is equal to 36.81 kJ/mole.

The activation enthalpy and entropy for the HDS process was calculated by using the following equation(23), which was obtained from the absolute rate theory.

$$\frac{k}{T} = K_T \frac{K_B}{h} \exp\left(\frac{\Delta S}{R}\right)\cdot\left(-\frac{\Delta H}{RT}\right) \tag{2}$$

A plot of ln (k/T) vs. (10^3/T) presented in Figure (18) gives a straight line with slope equals to $(-\Delta H/R)$ from which the activation enthalpy is 33.25 kJ/mole.

The intercept of these lines which is equal to $\ln\left(\frac{K_T\ K_B}{h}\right)+\frac{\Delta S}{R}$, from which the activation entropy ΔS is – 42.68J/mole. K.

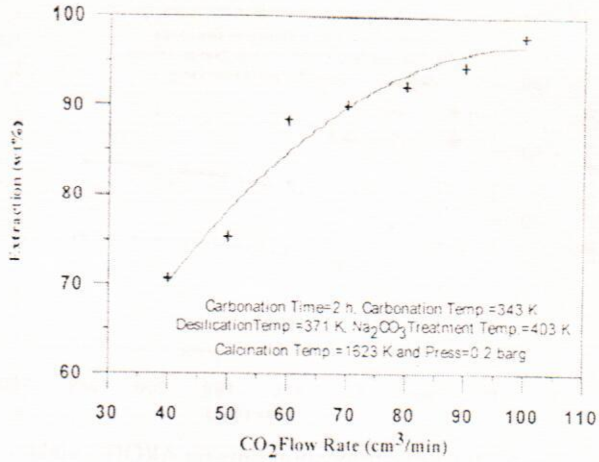

Fig. 2 Effect of CO_2 flow rate on $Al(OH)_3$ extraction from bauxite

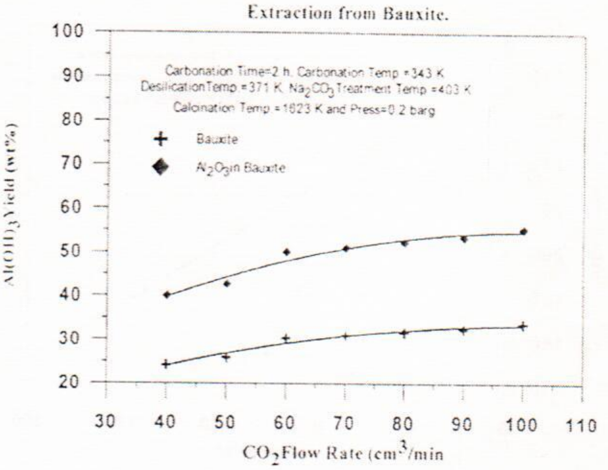

Fig. 3 Effect of CO_2 flow rate on $Al(OH)_3$ yield based on bayxite and Al_2O_2 in bauxite

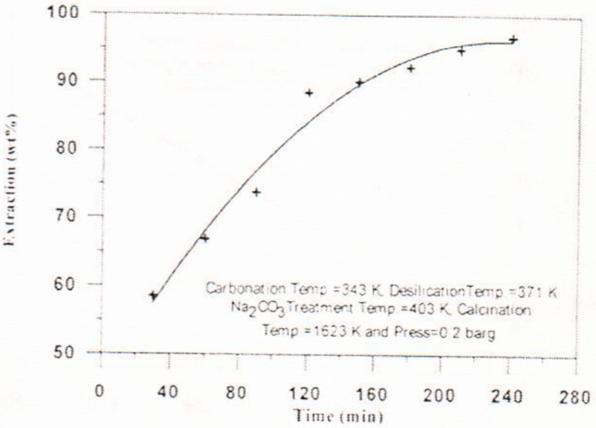

Fig. 4 Effect of carbonation time on $Al(OH)_3$ extraction from bauxite

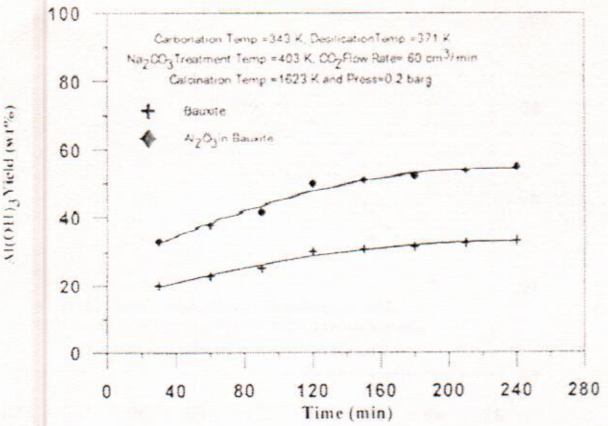

Fig. 5 Effect of carbonation time on $Al(OH)_3$ yield based on bauxite and Al_2O_2 in bauxite

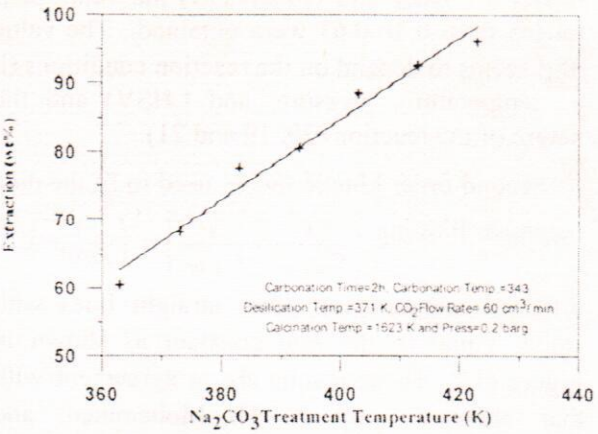

Fig. 8 Efect of Na_2CO_3 treatment temperature on $Al(OH)_3$ on extraction from bauxite

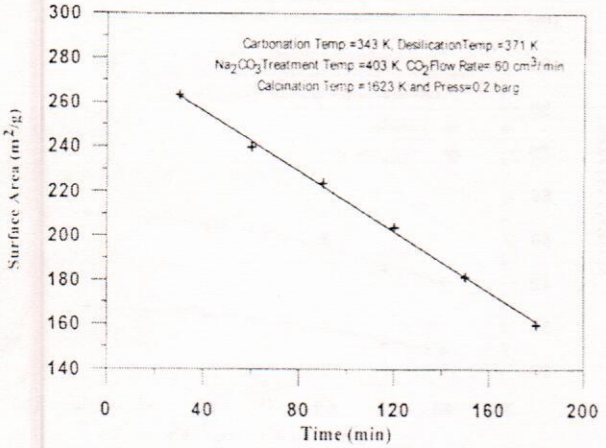

Fig. 6 Effect of carbonation time on surface area of gama-Al_2 on the extraction from bauxite

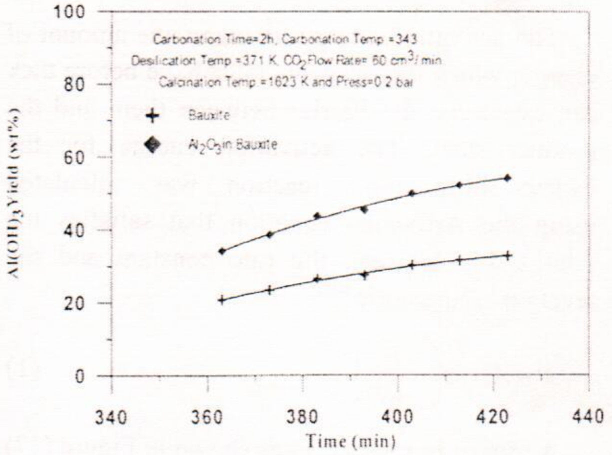

Fig. 9 Effect of Na_2CO_3 treatment temperature on $Al(OH)_3$ yield based on bauxite and Al_2O_3 in bauxite

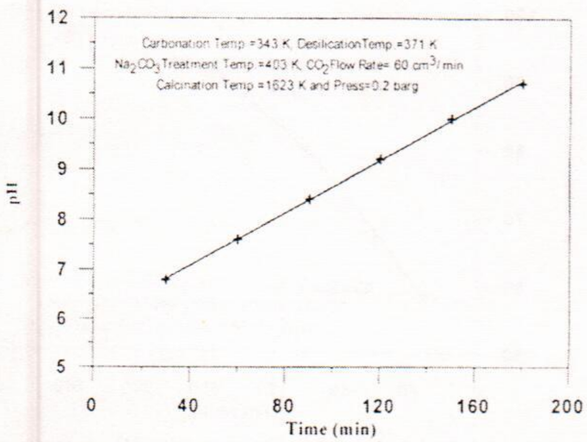

Fig. 7 Effect of carbonation time on pH of $Al(OH)_3$ on the extraction from bauxite

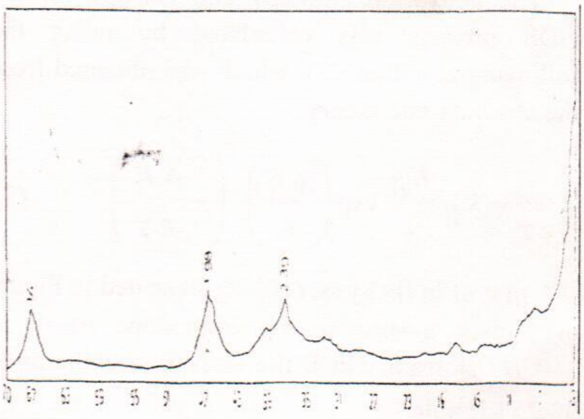

Fig. 10 X-ray of prepared γ-Al_2O_3 from bauxite

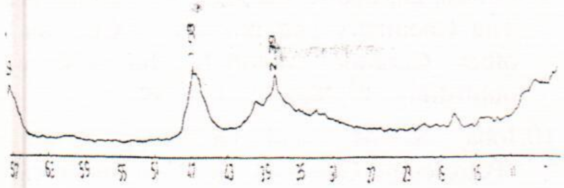

Fig. 11 X-ray of commercial γ-Al_2O_3 from bauxite

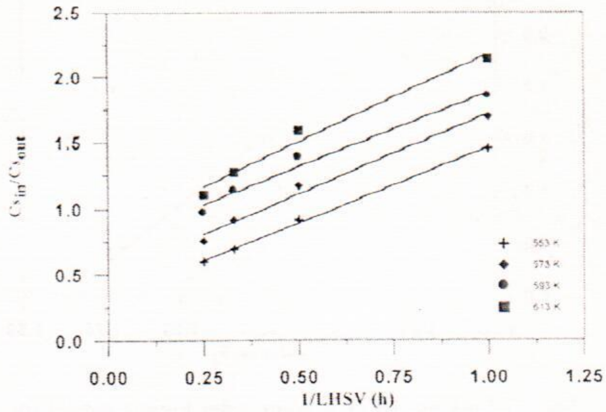

Fig. 14 First order kinetic model for HDS of gas oil using catalyst prepared from bauxite

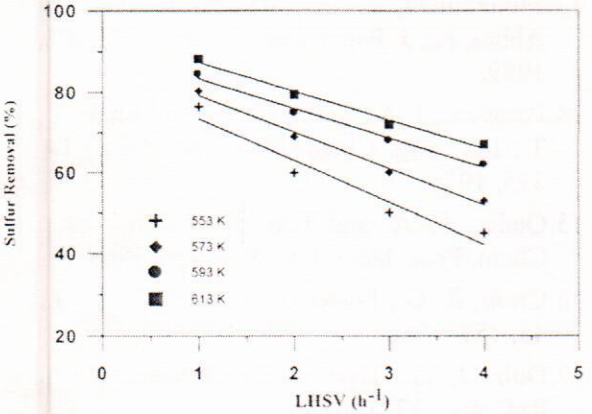

Fig. 12 Effect of LHSV on sulfur removal for gas oil at different temperature of industrial catalyst HT-500R

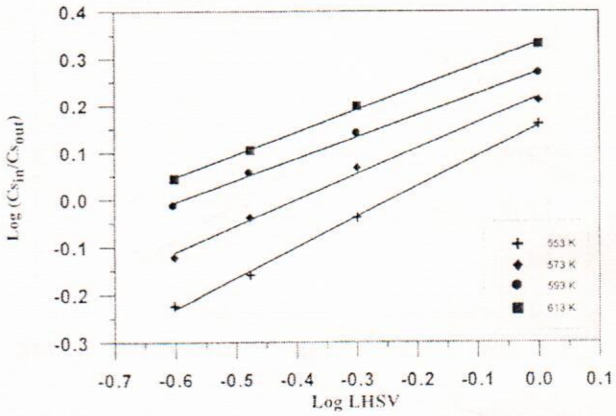

Fig. 15 Log-Log first order kinetic model for HDS of gas oil using catalyst prepared from bauxite

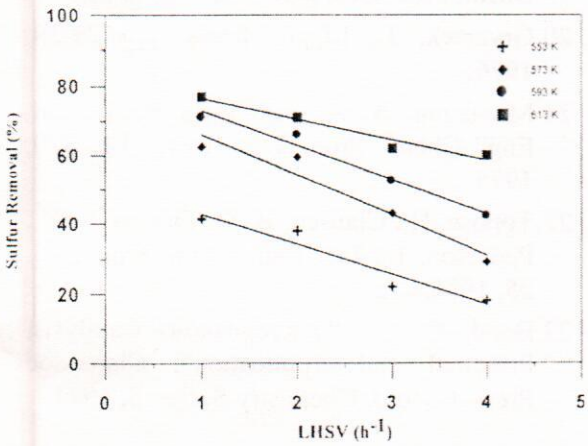

Fig. 13 Effect of LHSV on sulfur removal for gas oil at different temperature of industrial catalyst HT-500R

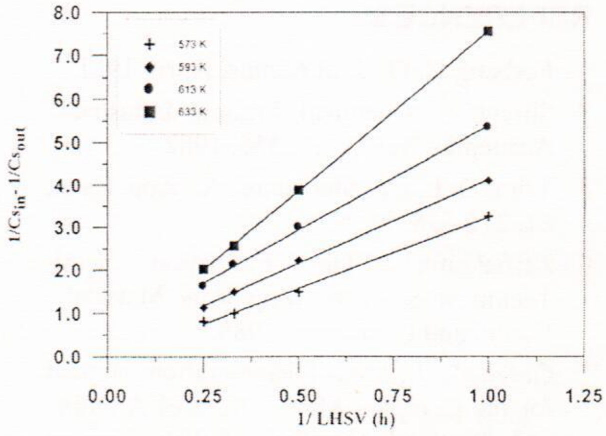

Fig. 16 Second order kinetic model for HDS of gas oil using catalyst prepared from bauxite

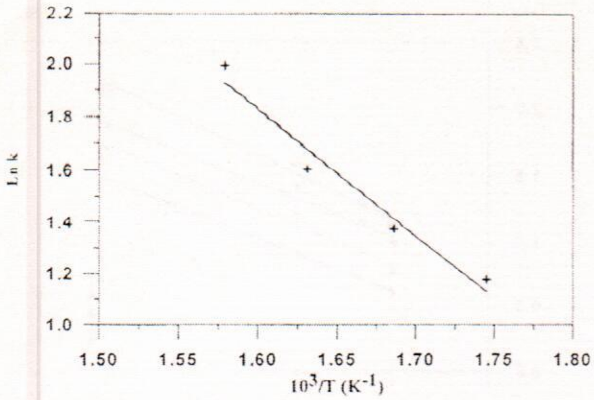

Fig. 17 Ln k vs. $10^3/T$ second order kinetic model for HDS of gas oil using catalyst prepared from bauxite

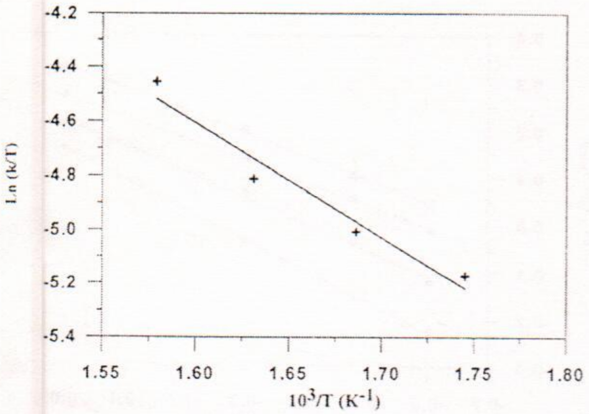

Fig. 18. Ln k vs. k/T second order kinetic model for HDS of gas oil using catalyst prepared from bauxite

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