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Recovery of the Components of Spent C18-HC Catalyst and Reuse Them to Prepare it

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Abstract

The components of C18-HC spent catalyst used for oxidation of CO to CO_2 in urea fertilizer industry were recovered using acid treatment and sulfide precipitation technique at different pH values, they were converted to copper nitrate, zinc nitrate and aluminum hydroxide. The efficiency of extraction approached 89.9 % for copper and 88.6 % for zinc with the purities of copper nitrate is 99.2 % and zinc nitrate to be 99.5 %. A new catalyst was prepared again from these recovered materials. Its physical and chemical properties were also determined and the structure characterized by X-ray diffraction spectroscopy.

Introduction

Processing of spent catalysts for winning their metal values [1] except for some noble metals based systems was in its infancy even fifty years ago. Most frequently used metals in the catalysts are critical ones such as cobalt, nickel, molybdenum, vanadium, copper, zinc etc in addition to noble metals. However there have been discouraging factors in the way of taking up the processing of spent catalysts for metals values. Some of these are:

1-Source raw materials are spread over a wide area
2-Transportation problems
3-Uncertain availability as life of catalysts varies.

4-Non-availability of standard processes for treating spent catalyst (unlike those of ores).

In spite of theses factors, there are always some driving forces for the recovery of metals from spent catalysts. Some of these factors are:

1-Conservation of natural resources .

2-Lower cost of recovered metals compared to virgin metals .

3-Non-availability of the metals indigenously .

4- Higher disposal cost due to anti-pollution regulations .

5-Shortage of disposal sites .

6-Minimizing environmental pollution .

$CuO-ZnO-Al_2O_3$ catalysts are very important for uses in industry [2,3]. Some of these catalysts are used in urea fertilizer industry for the conversion of CO to CO_2 in the presence of steam. Other types are used in methanol production units from the synthetic gas. These catalysts contain 30-45% CuO, 40-55 % ZnO and 10-20% Al_2O_3, when these catalysts loose activity and the successive processes of regeneration and activation failed to renew them, it is replaced by a new one and the spent one is discarded .

Owing to important of zinc and copper and their compounds and a wide spread uses in industry, a lot of works has been published regarding their recovery from industrial wastes and spent catalysts in particular. Zinc and copper were recovered from sulfide concentrates [4] by sulphate, acid washing and then purification and concentration. In brine washing [5] using $CaCl_2$ for separation of zinc and copper from hazardous industrial wastes, the separation was done at a pH of 2 and at 90 °C . Nickel and aluminium were recovered simultaneously [6] from spent reformer catalysts by treating it with caustic soda solution at temperature 90-100 °C with recovery of 97.4 %. The valuable metals were recovered [7] from Al_2O_3-based catalysts such as Co, Ni by leaching with 30% H_2SO_4 and 80 °C with a recovery of 98.2% for nickel and 98.5 % for cobalt.

Copper compounds:

Copper is one of the oldest known metals used by man, of its ores are [8,9] cuprite,Cu_2O.Chalcocite, Cu_2S , chalcopyrite,

$CuFeS_2$ malchite, $(CuOH)_2CO_3$, and bornite,Cu_5FeS_4.The oxidation states +1 and +2 reason for copper to have the catalytic activity.

Copper (I) nitrates: Unstable compound [8-10] which quickly and easily oxidized to cupric nitrate. It can be obtained by contacting copper nitrate (II) and ammonia solution with copper metal in the absence of oxygen and then evaporating ammonia to leave copper (I) nitrate.

Copper (II) nitrate: Blue crystals with [10] a melting point of 114.5 °C , easily soluble in water and ethanol, It can be obtained by dissolving the cupric oxide, carbonate or hydroxide or even copper metal in nitric acid.

Copper (II) sulphate: This salt exists as a series of compounds that differ in their degree of hydration. The anhydrous form is a pale green or gray-white powder, whereas the pentahydrate, the most commonly encountered salt, is bright blue. It is used as herbicide, fungicide and pesticide, analytical reagents, in organic synthesis and chemistry education [11-12].

Cupper sulfide (II): Hexagonal crystal structure with blue color, Insoluble in water and can be prepared industrially by precipitation from the reaction of copper salts with hydrogen or sodium sulfide in hydrochloric acid solution,

Zinc compounds:

Zinc is of relatively low abundance [13] in nature (of the order of 10-6 of the crust of the earth).The primary source of zinc is sphalerite, ZnS, goslarite, $ZnSO_4$ **.** $7H_2O_2$ wurtzite (Zn,Fe)S. At the current rate of consumption, the earth has been estimated to have 46 years supply of zinc remaining [14]. Methods of isolation involve flotation and roasting, which yield the oxide which is then reduced with carbon. The main use of zinc is iron galvanization, copper alloys to produce bronze and brass.

Zinc nitrate: Insoluble salts when pure and can not be obtained easily owing to the difficulty of separating the water of crystallization from the hydrated salts. The hexahydrate salts is colorless crystals with melting point of 36.4 ^oC and solubility in water of 1843 gm/Liter at 20 ^oC.

Zinc sulphate : Colorless orthorhombic crystals [9,15] and exists as monohydrate, hexahydrate and heptahydrate with the last one being the most predominant and is known as goslarite.

Zinc oxide: White powder and get yellowish when heated at elevated temperatures. Industrially it can be prepared from zinc metal evaporation or zinc oxide ores reduction to metal and then evaporation followed by roasting. It is used in purification of gases and the natural gas in particular from H_2S gas by adsorption of H_2S on its surface [16]. Also it is used in rubber and paints industry.

Zinc Sulfide: Exist as hexagonal structure and cubic one known as. Insoluble in aqueous solution and soluble in acid solutions with liberation of hydrogen sulfide. In air it oxidized slowly to sulphate .The man use of it is paint industry, x-ray screen, watches, and telecom and communication industries.

The aim of the present investigation is recovery of zinc, copper and aluminium from spent CuO-ZnO-Al_2O_3 catalyst and convert them to their compounds which were then reused in the preparation of the catalyst again.

Experimental

Material and methods

Materials:

Spent C18-HC catalyst, from Basrah urea production plant in ministry of Industry of Iraq.Sulfuric acid, nitric acid, acetic acid, ammonium hydroxide, H_2S gas. Sodium hydroxide, graphite analytical grade (>99% purity), were used. Zinc nitrate, $Zn(NO_3)_2$. 6H2O, cupper nitrate, $Cu(NO_3)_2$. $3H_2O$ and aluminium hydroxide $Al(OH)_3$ produced from the spent catalysts were used.

Spent catalyst calcinations:

The spent catalyst used in our study contains CuO, ZnO and Al_2O_3 with significant amount of carbonaceous and non-hydrocarbon materials, so it was calcined by roasting it in a furnace at 700 ^oC for four hours, this reduced the solid materials present in the catalyst from 5% to 1.5 %.

Elemental analysis:

Copper was analyzed by iodometric titration [17] whereas all other elemental determination was determined by standard atomic absorption method.

Separation of copper and zinc:

10 gm of calcined catalyst was extracted by refluxing with(3N) H_2SO_4 for five hours, then the extract filtered off to separate the left solid materials which may be present. The pH control method [17] was experimented to separate metals from the catalyst extract as sulfides since Cu precipitated as CuS in basic medium with pH of 9 and Zn can be precipitated as ZnS in slightly acidic one with pH of 6.The extract with pH of about one was used, it was heated with stirring to 100 ^oC and H_2S gas was passed through the solution for four hours where a black precipitate CuS is formed, The precipitate is collected and filtered off then treated with 40 % nitric acid with heating and stirring to convert it to copper nitrate which is washed with water , recrystallized and separated as $Cu(NO_3)_{2.}\ 3H_2O$.

The filterate from above was adjusted using ammonia solution to a pH of 3-3.8 and heated with stirring to 100^oC and then a current of H_2S gas was bubbled through for a period of four hours to obtain a white precipitate of ZnS. The precipitate is collected and filtered off then treated with 40 % nitric acid with heating and stirring to get zinc nitrate which is recrystallized and separated as $Zn(NO_3)_2.6H_2O$.

. Finally all the filterates left from the above processes were collected and treated with ammonia solution and the gel precipitate of aluminium hydroxide was collected.

Catalyst preparation:

The catalyst with the chemical composition weight of 43: 47: 10 for the three oxides CuO: ZnO: Al_2O_3 respectively was chosen to be prepared [18-20] because it is widely consumd, from zinc nitrate, copper nitrate and aluminium hydroxide recovered from the spent catalysts by using precipitation agent as sodium hydroxide. The precipitate was filtered off and washed

several times with distilled water until the pH of the filtrate reached 7.The solid was dried in an oven at 110^{o}C for 6 h to evaporate water. Finally it is calcined at 350^{o}C in furnace for 12 h.

Catalysts characterization**:**

For powder X-ray diffraction a Phillips X-ray diffractometer with CuKα radiation (1.542 ^{0}A , 40 kV, 20 mA) scanning over the range of angles of 3 to 70 on 2θ was used .Peaks were assigned by comparison with the d spacings of typical compounds given in the ASTM powder diffraction files [21].

Bulk density is determined by placing a weight catalyst in a graduated cylinder then shakes it by hand on the table or by vibrator and read the volume of it and then calculate the density. The particle density is measure by weighting a symmetrical tablet and calculates its volume. It is carried out for several tablets and takes the average. Pore volumes were determined by the liquid impregnation method. Hardness was determined with the ERWEKA TBH28 hardness meter.

Other mechanical properties were done according to procedures described by Richardson [22].Finally selected particle size was mixed with 1% graphite as binder and lubricant thoroughly and converted to 4mm x 6mm size tablets using a tablete machine.

Results and Discussion

The difficulties of three elements separation in such kind of waste catalysts is finding the suitable solvent that dissolve at once the three metals and providing also a suitable media to precipitate them quantitavely and with out interferences. Three acids were used for this purpose, (5N) HCl, (1.73N) acetic acid and (9N) H_2SO_4 using different weights of catalysts and a time of 5-6 h. The catalyst dissolved completely in all these acids but the latter seem to the most effective one. Experiments were done on (3N) H_2SO_4 which was also successful in dissolving the three metals as the left insoluble were 1 %, 1.5 for (9N), (3N) H_2SO_4 respectively.

Evaluation of results for copper recovery:

10 gm of spent catalysts was used in the experiment which contains 3.43gm, 3.77gm, and 0.53 gm of Cu, Zn and Al respectively.

Experimental weight of Cu in liquid extract is 3.08 gm

Theoretical weight of Cu in spent catalyst is 3.43 gm

Efficiency of extraction process 89. 9 %

Experimental weight of CuS obtained 4.27 gm

Theoretical weight of Cu as CuS 4.64 gm

Efficiency of precipitation process as CuS is 92.1 %

Experimental weight of $Cu(NO_3)_2$. 3H2O obtained is 10.29 gm

Theoretical weight of Cu as $Cu(NO_3)_2$. $3H_2O$ in spent catalyst is 10.83 gm

Efficiency of conversion from CuS to $Cu(NO_3)_2$. 3H2O is 95.01 %

Purity of $Cu(NO_3)_2$. $3H_2O$ obtained is 99.2 % determined from the chemical analysis

Evaluation of Results for Zinc recovery:

Experimental weight of Zn in liquid extract is 3.34 gm

Theoretical weight of Zn in spent catalyst is 3.77 gm

Efficiency of extraction process 88.6 %
Experimental weight of ZnS obtained 4.68 gm
Theoretical weight of Zn as ZnS 4.98 gm
Efficiency of precipitation process as ZnS is 94 %
Experimental weight of $Zn(NO_3)_2 . 6H_2O$ obtained is 13.61 gm
Theoretical weight of Zn as $Zn(NO_3)_2 . 6H_2O$ in spent catalyst is 14.33 gm
Efficiency of conversion from ZnS to $Zn(NO_3)_2 . 6H2O$ is 94.97 %
Purity of $Zn(NO_3)_2 . 6H_2O$ obtained is 99.5 % determined from the chemical analysis

For aluminium the aluminium hydroxide was collected and analyzed for aluminium content and not recrystallized because it is gelatinous and hydrous in nature and is used as it is in preparation.

The calculated extraction efficiencies for copper, 89.9 % and zinc, 88.6 % are reasonably good for these catalysts which is used for long time in oxidation process and resulted to reduction of some zinc and copper compounds to free metals which may undergo volatilization in addition to the formation of stable carbonaceous material that can not be dissolved easily. Also some metal oxides such as those of iron resulted from corrosion in side the reactor may interfere.

The precipitation as sulfides efficiencies of 92.1 % for Cu and 94 % for Zn and as nitrates with 95.1% for Cu and 94.97% for Zn is high and encouraging with the compounds being obtained with a good purity. When recycled for the preparation of the same catalyst system, normally metals need not be recovered in the purest form [1] thus reducing the process-steps and the cost of production to a large extent. These results encouraged as to go further and use them in the preparation of the catalyst again.

X-ray diffraction spectra of prepared catalyst confirm the structure as shown by Fig.1.The results show the presence of CuO ZnO as separate oxide in addition of being fused mixed oxide with Al_2O_3 [23]. The surface and mechanical properties of the prepared catalyst in addition to the pore volume and density measurement of the prepared catalyst is given in table (1) demonstrated the similarities between the commercial and prepared catalysts with slight differences that is considers to be within the experimental errors

of recovery process of several steps and taking into account that we used recovery materials and not pure one

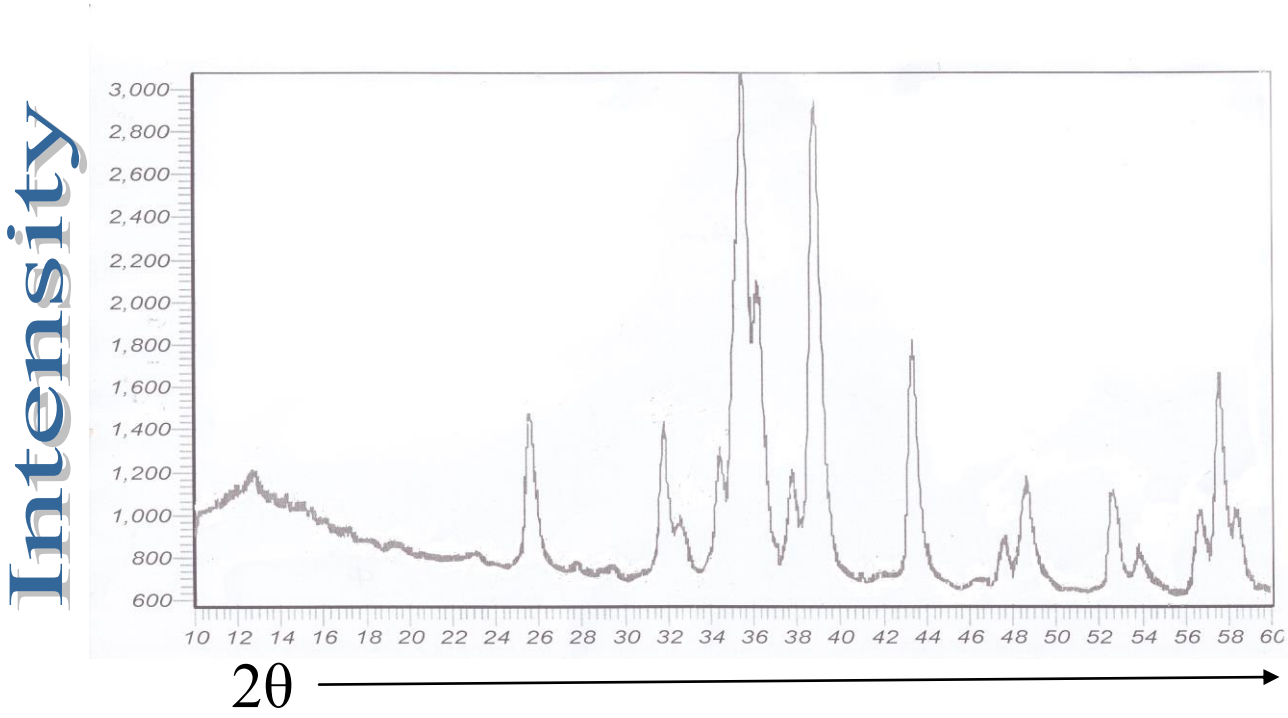

Fig. 1. X-ray diffraction patterns of the prepared CuO-ZnO-Al_2O_3 catalyst

Table (1).Physical and chemical properties of the prepared and commercial C18-HC catalysts.

properties	Catalysts	
Composition / wt %	Prepared	Commercial
CuO	43.1	43
ZnO	47.3	47
Al_2O_3	9.6	10
Cu	34.38	34.29
Zn	37.94	37.71
AL	5.08	5.29
Pellete size/mm	4x6	4x6
Particle density / gcm^{-3}	3.65	3.56
Bulk density / gcm^{-3}	1.06	1.08
Surface area / $m^2.g^{-1}$	73	78
Pore volume / cm^3g^{-1}	0.33	0.35
Hardness / kg	8.5	8.3
Loss on ignition / wt%	11	12
Loss on attrition / wt%	0.21	0.14

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أسترجاع مكونات العامل المساعد C18-HC واستخدامها في أعادة تحضيره

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الخلاصة:

تم العمل على استرجاع مكونات العامل المساعد C18-HC المستعمل في أكسدة أحادي أوكسيد الكاربون الى ثنائي أوكسيد الكاربون في معامل صناعة أسمدة اليوريا بطريقة المعاملة الحامضية وتقنية الفصل والترسيب على شكل كبريتيدات باستعمال دالات حامضية مختلفة. حولت المركبات المسترجعة إلى نترات النحاس ، نترات الخارصين وهيدروكسيد ألألمنيوم حيث كانت كفاءة الفصل للنحاس % 89.9 وللخارصين % 88.6 في حين كانت نقاوة نترات النحاس % 99.2 ونترات الخارصين % 99.5 . استعملت هذه المواد في أعادة تحضير العامل المساعد ثانية.حددت الخواص الفيزياوية والكيماوية للعامل المساعد المحضر و درس تركيبه بواسطة طيف حيود ألأشعة السينية.