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PREPARATION AND ACTIVITY TEST OF THE CATALYST USED IN CARBON DIOXIDE LASER OF SEALED TUBE

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ABSTRACT

A new catalyst composing of a mixture of CuO-ZnO-Al_2O_3 was prepared. Testing of it in a pilot plant showed that it can be used in the oxidation of CO to CO_2. Using of the catalyst in the sealed CO_2 laser unit indicated that it is very useful in this respect as the laser reserved its activity and power.

Key words : Catalyst, Sealed CO_2 laser, Carbon monoxide oxidation Activity , X-ray diffraction

تحضير وفحص فعالية العامل المساعد المستخدم في ليزر ثنائي اوكسيد الكاربون ذو ألأنبوبة المغلقة

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الخلاصة

تم العمل على تحضير عامل مساعد يتكون من نسب معينة من اوكسيد النحاس- اوكسيد الخارصين واوكسيد ألألمنيوم. أجريت عملية فحص للعامل المساعد باستخدام وحدة ريادية لهذا الغرض حيث بينت النتائج إن العامل المساعد يتمتع بكفاءة عالية لتحويل أحادي اوكسيد الكاربون إلى ثنائي اوكسيد الكاربون.أظهرت نتائج استعمال العامل المساعد في وحدة ليزر ثنائي اوكسيد الكاربون المغلقة امكانية استعماله مع المحافظة على القدرة الجيدة والمطلوبة لليزر.

INTRODUCTION

The active medium in the CO_2 laser is a mixture of carbon dioxide, nitrogen and helium with volume composition of (9.5% CO_2, 77% He and 13.5 % N_2). In sealed-tube laser Hecht described that the discharge gases are completely sealed within the discharge tube. The problem with this arrangement, as far as the CO_2 laser is concerned is that during discharge conditions the CO_2 tends to break down into CO, so if no precautions were taken, lasing would ceased after few minutes. One solution is to add hydrogen or water vapor to the gas mixture, to react with the CO and regenerate CO_2 other is by using catalytic action (Wilson and Hawkes).

Several catalysts were experimented for this type of oxidation coming from supported metal catalysts Pd/SnO_2 , Pt/SnO_2 and Pt/SiO_2 to precipitated catalysts $Cu/Cu_2O/CuO$ (Bond et.al) , (Fuller and Warwick). It was observed that using 1.5 g of catalyst with 2% Pt supported on SnO_2 at a temperature of 60 °C and gas flow rate of 10 ml min^{-1} resulted in 98-100 % efficiency for 318 hour. As far as the effect of Pt content in the catalyst on efficiency is concerned it seem that 2% Pt catalyst showed doubled efficiency of that catalyst which composed of 1% Pt. On the other hand 1% Pt and 1% Pd bimetallic catalyst supported on SnO_2 reflect a higher efficiency.

Generalov et.al used application of distributed gold catalyst to increase output power and efficiency of a sealed off CO_2 laser.

$CuO-ZnO-Al_2O_3$ catalysts are very important with widespread uses in industry. Some of these catalysts are used in urea fertilizer industry for the low temperature, 180-260 ℃ conversion of CO to CO_2 in the presence of steam, the reaction known in industry as Low Temperature Water Gas Shift Reaction (LTS), (Ronald.F.Mann and et.al). Other types are used in methanol production units from CO/H_2 mixture at low pressure of 70 bar and a temperature of 220-240 °C (T.V.Herwwinen and W.A.De Jong).

The aim of the present investigation is to prepare a new and suitable catalyst that can oxidize CO to CO_2 and can be used in a sealed CO_2 laser so that it can replace the one in the discharge tube after being loose its activity.

EXPERIMENTAL

CATALYST PREPARATION

Zinc nitrate, $Zn(NO_3)_2$., cupper(II) nitrate, $Cu(NO_3)_2.6H2O$, sodium bicarbonate, $NaHCO_3$, poly vinyl alcohol, PVA, graphite and aluminum oxide, Al_2O_3 analytical grade (>99% purity), were used.

The catalyst with the chemical composition weight of 32 : 53 : 15 for the three oxides CuO : ZnO : Al_2O_3 respectively was prepared from zinc nitrate, copper nitrate and aluminum oxide and using the precipitation agent as sodium bicarbonate.

Aluminum oxide was placed in a suitable size beaker, copper nitrate solution was prepared by dissolving copper nitrate in distilled water and zinc nitrate solution was prepared by dissolving zinc nitrate also in distilled water , these two solutions were mixed together and added to the aluminum oxide powder to form solution ready for precipitation process. Precipitating agent solution, one molar sodium bicarbonate in distilled water was prepared . The precipitating agent was added to nitrates solution above gradually with continuous stirring at a temperature of 60-80 ^{o}C. The pH of the solution at the beginning was 2 and the precipitation will be completed (Boreskov G.K) when the pH reaches 6.8. The precipitate was left overnight to settle and then the solution tests for complete precipitation. 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 120 ^{o}C for 6 h to evaporate water. Finally it is calcined at 350 ^{o}C in a furnace for 12 h.

CATALYST PELLETING

The calcined catalyst powder was mixed with a solution of polyvinyl alcohol (3%) in distilled water. The paste so produced was then dried at 110 ^{o}C for 2 hours and then the temperatures raised to 225 ^{o}C and kept for another 2 hours and finally the catalyst was crushed and sieved to get the 1mm size. Pellets (or tablets) (7 mm diameter, 4 mm thick) were prepared in a tablet press at 2 atm. The pellets were calcined at 500 ^{o}C to dissociate the polyvinyl alcohol.

CATALYST CHARACTERIZATION

Cu, Zn and Al were determined by standard atomic absorption methods. For powder X-ray diffraction a Phillips X-ray diffractometer with CuK_{α} radiation (1.542 Å, 40 kV, 20 mA) scanning over the range of angles of 3 to 70 on 2 .Peaks were assigned by comparison with the d spacings of typical compounds given in the ASTM powder diffraction files.

Pore volumes and densities were determined by the liquid impregnation methods described by Richardson. Hardness were determined with the ERWEKA TBH28 hardness meter.

The Bulk density is determined by placing a weight catalyst in a graduated cylinder then shake it by hand on the table or by vibrator and read the volume of it and then calculate the density i.e it is the packing or load density of the reactor. The solid density is measure by weighting a symmetrical tablet and calculate it s volume. It is carried out for several tablets and take the average.

CATALYST TESTING

The feed was obtained by mixing the gas mixture obtained from the Baji fertilizer company with N_2 to get the volume composition of 25 : 60 : 15 for CO : H_2O : N_2 respectively.

Continuous flow pilot plant (Fig. 1, 2). The reactor was stainless steel (316-heat resistant), length 800 mm, inside diameter, 19 mm. Heaters were in the form of four separately heat-controlled block shells. The reactor was packed with 110 ml of the catalyst between two layers of inert material such as glass, inert alumina or porcelene balls. Catalytic tests were performed operating at a temperature of 200 °C, 250 °C, 300 °C and 350°C and pressure of 1.2 Mpa and using space velocities of 15000 h^{-1}.

In a typical run the reactor was purged with N_2 gas and the temperature raised. Since the catalyst works in a reduced form it was activated by heating to 200 *°C* in a nitrogen flow at a rate of 88 ml h^{-1}. Reduction was accomplished in 4-10 h using an activation gas consisting of 1-5 % H_2 in nitrogen at a temperature of 350 °C and pressure of 35 bar. After reduction and establishing steady state conditions, the feed gas mixture was pumped upwards into the reactor. The products passed to the gas flow meter for volume measurement and then for gas chromatographic analysis.

Testing the catalyst in the laser unit was done according to (Stark D.S et al) by introducing and distributing several tablets of the catalyst across the laser discharge tube , sealing it again, filling it with the discharge gas mixture. The laser is then operated at 30 kV starting voltage and 10 kV operating voltage, 7-25 mA tube current to give an output power of 35W and beam diameter of 1.5-2 mm.

ANALYSIS F THE GASEUS MIXTURE

Gas chromatographic analysis were done for the feed gas and all the produced gases using Perkin Elnmer type Sigma 30 Gas Chromatograph with flame ionization detector and molecular sieve type 5A as a stationary phase according to the procedure described by (Herwijnen.T.V and De Jong .W.E).

RESULTS AND DISCUSSION

The properties of the prepared catalyst represented in table (1) declare that it is similar to the commercial one in both physical and chemical properties. There is little differences in the chemical composition which may be attributed to some loss during the preparation steps , it may be also due to the presence of dehydrated water in the structure of salts used in preparations.

X-ray diffraction spectroscopic studies of prepared and commercial catalysts confirm their structures as their composition and physical properties are closest and they are structurally similar as shown by (Fig. 3). The X.-ray spectra identification (Gaydon, A. G., & Pearse, R.W.B) show the presence of CuO and ZnO as separate oxide in addition of being fused mixed oxide.

The surface and mechanical properties of the prepared catalyst in addition to the pore volume and density measurements encouraged us to test the catalyst performance and activity.

Table (2) shows the measurements of the activity and selectivities for the oxidation of CO to CO_2 represented as vol % CO_2 in the produced gas which is carried out at a temperatures of 200 °C, 250 °C, 300 °C and 350°C and pressure of 1.2 Mpa .and using space velocity of 15000 h^{-1}.

We take the activity as the percentage of CO converted to all products and the selectivity as the fraction of CO_2 in the products, i.e. CO_2 produced divided by CO converted (Satter F and Charles N).The aim in the catalysis is to maximize both the conversion and the selectivity at the lowest reaction temperature. In the experiments reported here we have attempted to optimize the catalyst and to compare the properties of the prepared catalyst with a commercial one.It is clear that the activity increased with temperature and reaching a value of 95.6 at 350°C.Also higher selectivities were obtained at higher temperatures where values can be obtained at temperatures of 300°C and 350°C of 87.6, 9.6 for activity and 98.6, 98.3 for selectivity respectively. The decreased in selectivity is due to the formation of by products at higher temperatures and catalyst effect, so we can see that the catalyst can be operated with a good activity and selectivity at 300-350 °C.

The catalysts was tested continuously for a period of 250 h and at different time intervals 50 h and shown it was maintaining a constant activity and selectivity.

Results of testing the catalyst in the laser unit **(Stark, D.S. et al**) with the power of the laser being monitored with time shows that its maintain good beam quality and constant output power during long duration time of continuous and non continuous operation as the laser seem to reserved 95-98 % of its original power, a value which is accepted in most sealed laser as mentioned by O'Halnon. Of most important benefit of the results is that we do not need to send the tube to the laser manufacturer after being loose the laser activity, a process which is financially expensive and time consuming in addition of the knowledge of the know how of this type of catalysts.

Table (1) : Chemical composition and physical properties of the prepared and commercial catalysts.

Catalyst Properties	Prepared catalyst	Commercial*
Composition / wt %		
CuO	32.2	32
ZnO	53.1	53
Al_2O_3	14.7	15
Cu	26.47	25.5
Zn	42.6	42.5
Al	7.78	7.9
Color	deep brown	deep brown
Pellet size/mm	7mmx4mm	7mmx4mm
Surface area /m^2 g^{-1}	75	70
Pore volume cm^3 g^{-1}	0.30	0.32
Solid density/g cm^{-3}	0.53	0.50
Bulk density /g cm^{-3}	1.05	1.10
Loss on ignition %	14	13
Loss on attrition %	0.11	0.12
Hardness /Kg	8.2	8

* From Baji urea production plant in ministry of industry of Iraq

Table (2) : The effect of temperature on the chemical composition of the feed.

Composition vol. %	Feed	Operating and testing temperatures, °C.			
		200	250	300	350
CO	25	18.5	3.8	3.1	1.1
H_2O	60	44.5	5.2	1.9	0.9
N_2	15	15	15	15	15
CO_2	0	6	17.3	21.6	23.5
H_2	0	13.8	55.7	58.4	58.5
Others	0	2.2	3	0	1
Activity	0	26.0	84.8	87.6	95.6
Selectivity	0	92.3	81.6	98.6	98.3

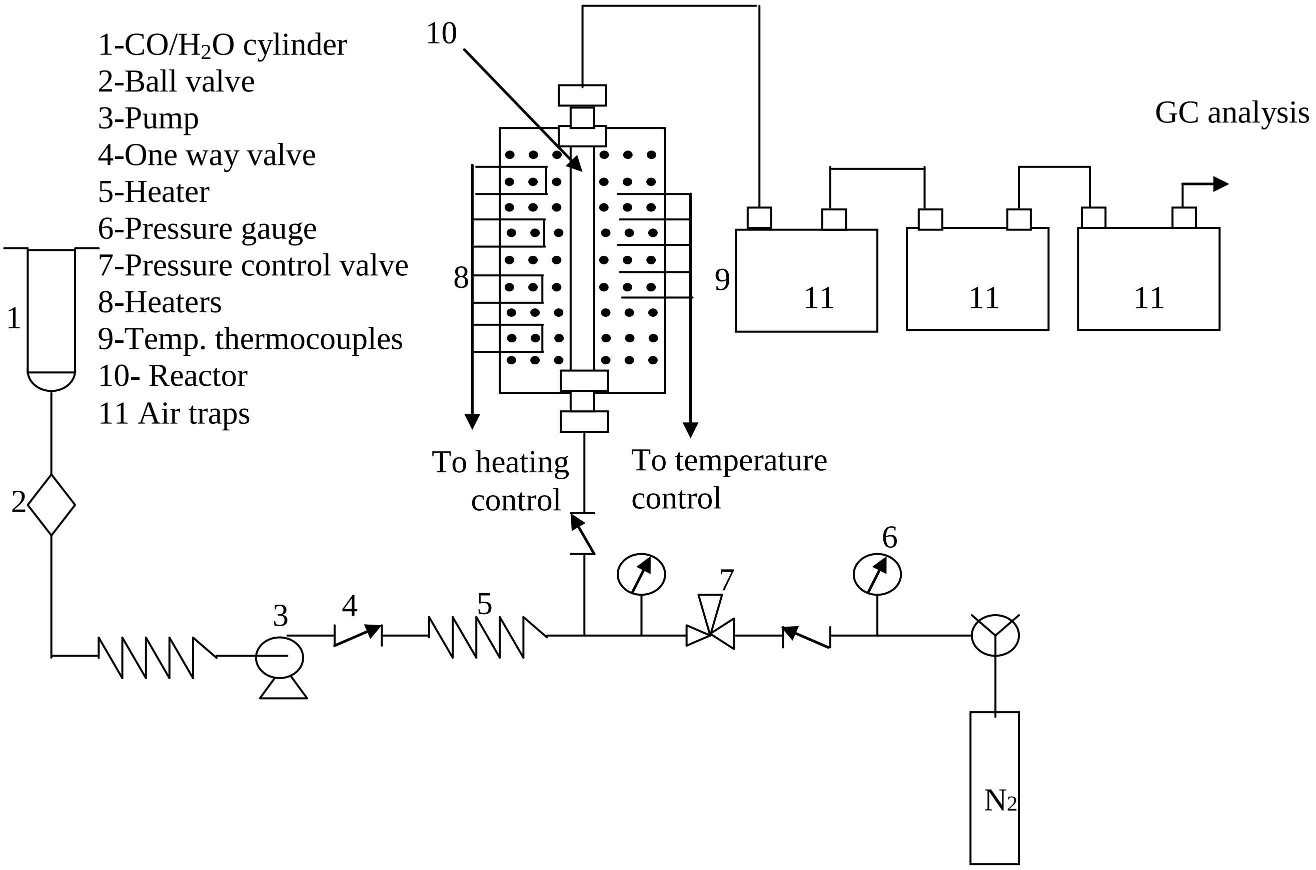

Fig.1. Flow diagram of laboratory testing unit

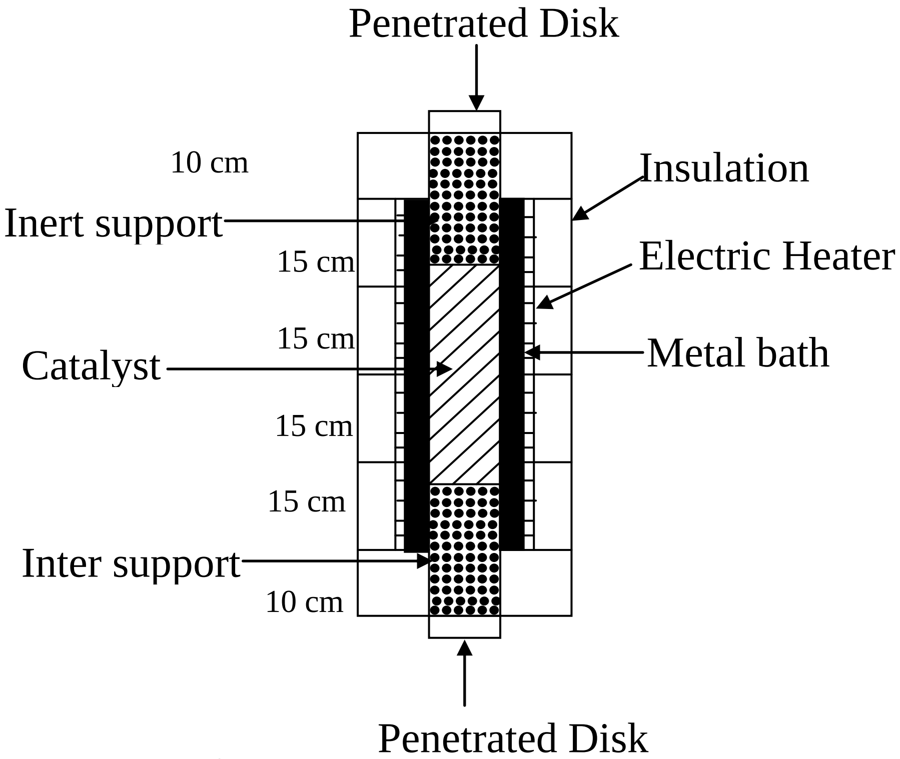

Fig.2. Front view section of the tubular reactor

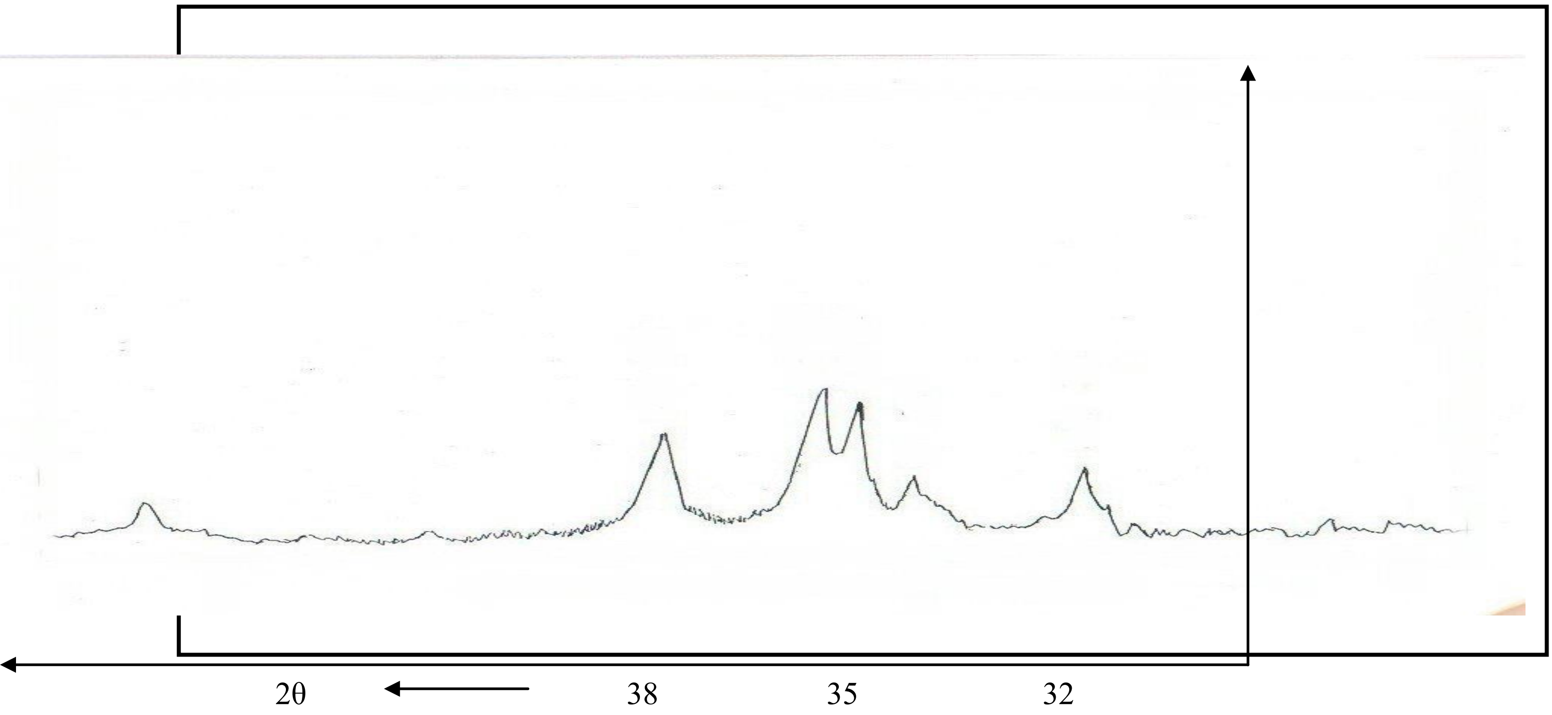

Fig. 3. X-ray powder diffraction patterns of the prepared $CuO\text{-}ZnO\text{-}A_{l2}O_3$ catalyst

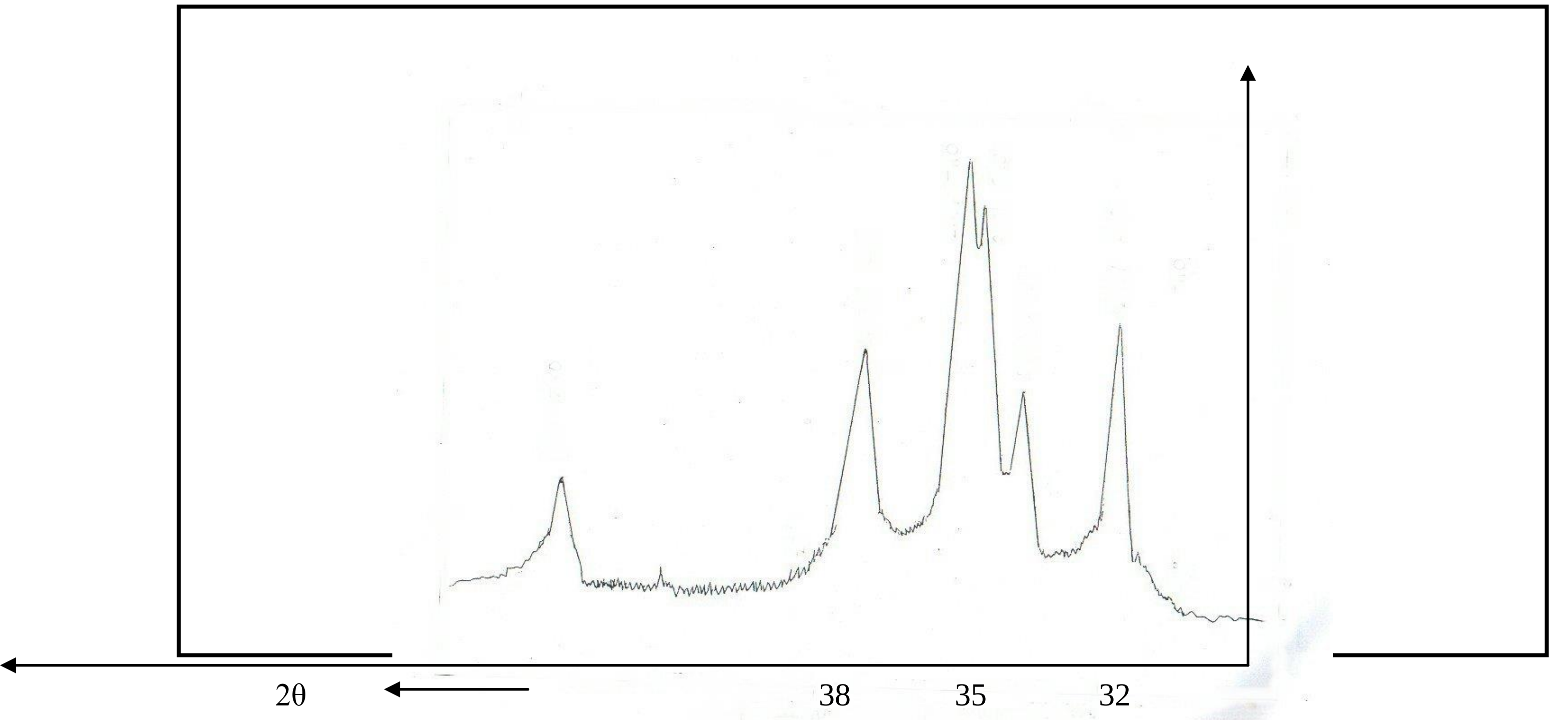

Fig. 3. X-ray powder diffraction patterns of the commercial $CuO\text{-}ZnO\text{-}Al_2O_{33}$ catalyst

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