

## Characterization of CuO-Kaolin Solids Used for Co-oxidation

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Six samples of copper oxide/kaolin were prepared by impregnating kaolin with solution containing different concentrations of Cu-nitrate. The obtained solids were thermally treated at different temperatures. The thermal products were characterized by XRD-analysis and were tested in the oxidation of carbon monoxide.

The results of X-ray investigation revealed that, supported metal oxide on the surface of kaolin appeared as crystalline oxide in the X-ray diffractogram. Solid-solid interaction occurred between the oxide and the decomposition products of kaolin yielding aluminate  $\text{CuAl}_2\text{O}_4$  and  $\text{CuAl}_2\text{O}_4\text{-Al}_2\text{O}_3$  solids solution. The prepared solids were tested in the oxidation of carbon monoxide. The results of the effect of calcination temperature on the activity revealed that catalysts activated at  $350^\circ\text{C}$  were more active than those activated at  $550$  or  $750^\circ\text{C}$ . The low activity may be attributed to the interaction between CuO and the thermal decomposition products of kaolin and/or sintering of the heated solid. The catalytic activity increased with increasing the metal oxide content in the catalyst and also with increasing the reaction temperature. The presence of oxygen (air) prevents the appearance of monovalent copper or metallic copper. This is because the reduced forms of copper are oxidized as fast as they formed.

### INTRODUCTION

The problem of protecting the environment from pollution and contamination by various types of discharges is now the focus of attention all over the world. The principal sources of harmful effluents to the atmosphere are heat power plants, automobiles and industrial plants. There are many methods that are used for gas purification. The catalytic gas purification is one of the most important methods and is based on the catalytic reaction by which pollutants are converted into other compounds. The toxic substances are not separated from the gas stream, but are converted into compounds whose presence in the atmosphere is permissible.

The most important of the positive features of the catalysis technique is the possibility of achieving a very high degree of gas purification, in some cases as high as 99.9%.

The catalytic oxidation of carbon monoxide efficiently takes place on various transition metal oxides such as  $\text{Cu}_2\text{O}$ , CuO, NiO,  $\text{Co}_3\text{O}_4$  and others<sup>1-4</sup>.

### EXPERIMENTAL

Copper nitrate was used in our investigations and was obtained from Merck

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Company (Germany). Egyptian Dehisa kaolin ore was used as a support in catalysts preparation.

**Catalysts preparation:** The catalysts were prepared by impregnating kaolin with a solution containing the appropriate concentrations of Cu-nitrate. The obtained solids were dried followed by homogenization, grinding and heating at 250°C for several hours till cessation of gases. The products were thermally treated by gradual increase of temperature up to 350°C and kept at that temperature for 4 h. The same heating process was performed at temperatures 550, 750 and 1000°C. The composition of different prepared catalyst solids are as follows:

1:1, 1:2, 1:3, 1:4, 1:8 and 1:16 (molar ratios) with respect to CuO : kaolin.

**X-ray analysis:** X-ray powder diffraction patterns were obtained at room temperature using a Philips X-ray diffractometer (Goniometer PW 1050/25) employing Ni-filtered Cu-radiation ( $\lambda = 1.50404 \text{ \AA}$ ). The X-ray tube was operated at 36 kV and 16 mA; the samples were packed into a plastic holder, no adhesive or binder was necessary. Spectra were scanned at a rate  $2^\circ \text{ min}^{-1}$  in  $2\theta$ .

**Flow system:** All tests of catalytic activity were carried out in a flow system. A silica tube reactor of 10 cm length and 2 cm inner diameter was introduced into another long silica tube which was heated by a tube furnace. The reactor was charged with 1 g catalyst in each experiment. The processes of catalysis were conducted at temperatures 230–320°C. The space velocities of reactants (3% CO + air) were varied between 5000 and 12000  $\text{h}^{-1}$ . The produced gases were analyzed quantitatively by conventional method, *i.e.*, by interacting the formed carbon dioxide with soda asbestos. Gas chromatography was also employed for gas analysis.

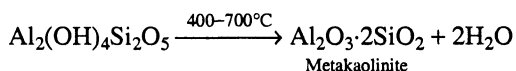
## RESULTS AND DISCUSSION

### Characterization of raw materials and the prepared catalysts

**Characterization of Kaolin:** The chemical analysis of kaolin ore is given below:

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Loss %
%	47.00	33.73	0.96	2.20	2.22	1.01	0.70	0.4	12.12

The X-ray analysis of Dehisa kaolin (Fig. 1) revealed that it is composed of various crystalline minerals in addition to kaolinite mineral. The minerals are anatase (TiO<sub>2</sub>), dolomite (MgCa(CO<sub>3</sub>)<sub>2</sub>) and orthoclase (KAlSi<sub>3</sub>O<sub>8</sub>). The effect of thermal treatment on the structure of kaolin has been investigated. It has been found that at about 100°C, the sorbed water is removed. On further increase of temperature, kaolinite undergoes dehydration (400–700°C). At this temperature kaolin is transformed into metakaolinite of amorphous structure:



The X-ray analysis of the original kaolin (Fig. 1) revealed that it is composed of kaolinite, some other minerals such as anatase ( $\text{TiO}_2$ ), dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ) and orthoclase ( $\text{KAlSi}_3\text{O}_8$ ). After thermal treatment at  $500^\circ\text{C}$ , the product was almost amorphous.

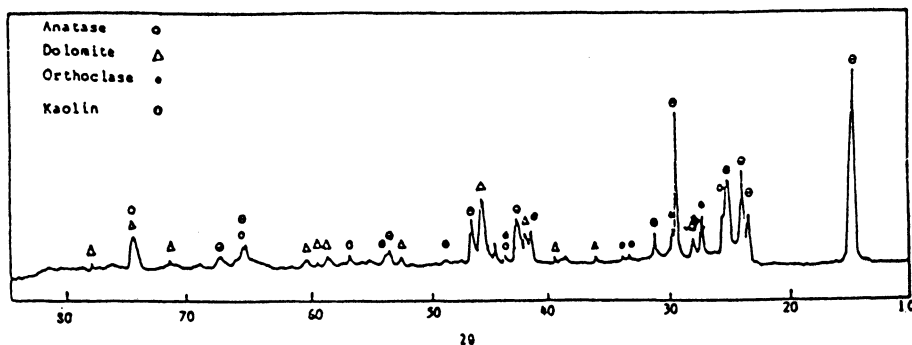
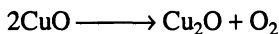
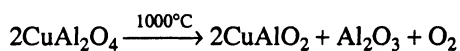


Fig. 1 X-ray diffraction patterns of Dehisa kaolin ore.

*Characterization of the prepared catalysts mixture of different molar ratios of CuO supported on kaolin:* The X-ray diffractograms of the prepared and preheated at  $350$ ,  $550$ ,  $750$  and  $1000^\circ\text{C}$  solids are presented in Figs. 2–5. It can be seen that the increase of concentration of metal oxide in the catalysts is accompanied by an increase in the intensity of X-ray diffraction patterns of the crystalline metal oxide with noticeable decrease in the intensities of the lines of kaolin. The increase of calcination temperature showed a detectable decrease in the intensity of X-ray diffraction patterns of crystalline CuO. This decrease in the intensities may be attributed to the solid-solid interaction between CuO and the thermal decomposition products of kaolin leading to the formation of amorphous or poorly crystalline phases. Sample was thermally treated at  $1000^\circ\text{C}$ ; besides CuO crystalline phase, it showed other crystalline compounds. These compounds may be formed as a result of reduction of CuO into  $\text{Cu}_2\text{O}$ ,



or the formation of a complex copper aluminate,



*Catalytic oxidation of carbon monoxide:* Reaction at atmospheric pressure in flow system on catalysts containing metal oxide supported on kaolin: Oxidation of carbon monoxide was performed in flow system and at atmospheric pressure with oxygen (air). The percentage of carbon monoxide in the gas mixture was 3% by volume. The experiments were classified into series according to the

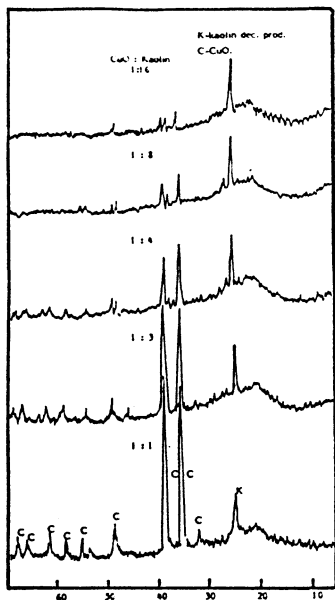


Fig. 2 X-ray diffraction patterns of catalysts containing CuO supported on kaolin with different molar ratios and preheated at 350°C.

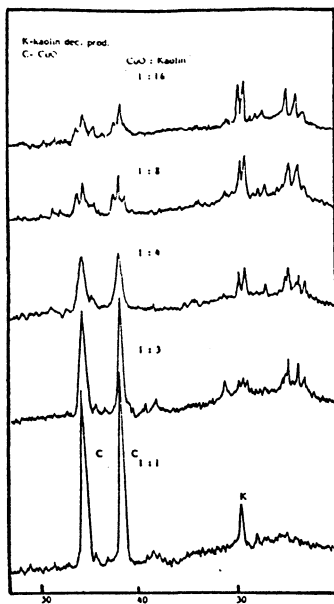


Fig. 3 X-ray diffraction patterns of catalysts containing CuO supported on kaolin with different molar ratios and preheated at 550°C.

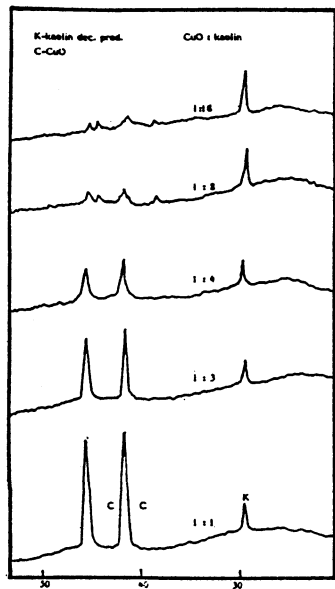


Fig. 4 X-ray diffraction patterns of CuO/kaolin for different molar ratios calcined at 750°C.

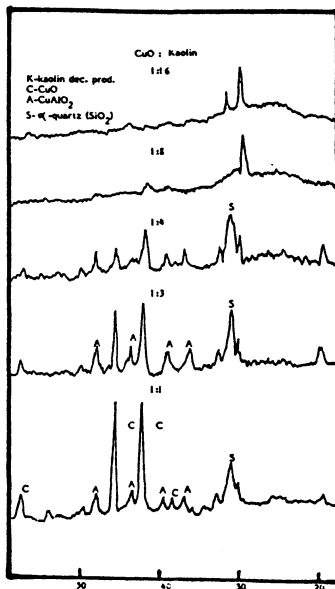


Fig. 5 X-ray diffraction patterns of catalysts containing CuO supported on kaolin with different molar ratios and preheated at 1000°C.

conditions of these experiments, *i.e.*, catalysts composition, calcination temperatures, reaction temperatures, space velocities, etc.

*The effect of catalysts composition on their activities in CO-oxidation:* A series of experiments was performed on catalysts calcinated at 350°C, for 4 h at a constant reaction temperature 230°C and space velocity 9000 h<sup>-1</sup>. The results of experiments on CuO/kaolin are listed in Table-1. It can be seen from Table-1 that the increase of metal oxide content increases gradually the activity of catalyst. This means that the process of catalysis may proceed on CuO or/and Cu aluminates formed by the combination of CuO with aluminum oxide produced from kaolin.

*The effect of calcination temperature:* In this case a series of experiments has been done to select the suitable calcination temperature for conducting the oxidation of carbon monoxide. The experiments were carried out at a constant reaction temperature 230°C and space velocity 9000 h<sup>-1</sup>. The results of the effect of calcination temperature on the activity of catalysts are listed in Table-1 and illustrated on Fig. 6. It can be seen that the calcination of catalysts at 250°C was the most effective temperature at which the percentage of oxidation was maximum. The increase of calcination temperature up to 550°C was accompanied by a decrease in the activity of catalysts. The activation of solids at 750°C showed

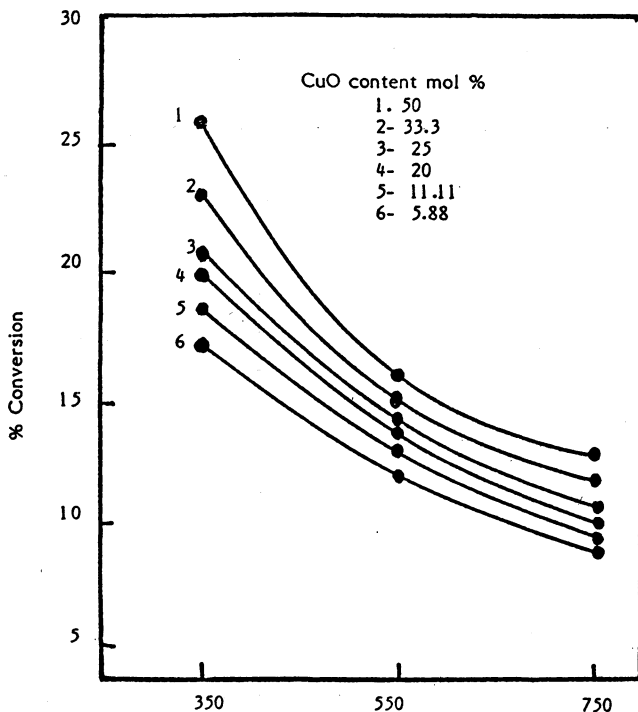


Fig. 6 Effect of calcination temperature on the activity of CuO/kaolin catalysts at reaction temperature 230°C, space velocity 9000 h<sup>-1</sup>

further decrease in the activities of catalysts. This decrease in activity may be attributed to the process of sintering and the interaction of metal oxide with the thermal products of kaolin leading to the formation of less active species.

TABLE-1  
THE EFFECT OF COMPOSITION OF CATALYSTS ON THEIR ACTIVITIES IN CO-  
OXIDATION (REACTION TEMPERATURE 230°C AND SPACE VELOCITY 9000 h<sup>-1</sup>)

Molar ratio CuO = Kaolin	Mol % CuO	Percentage of conversion on catalysis calcined at	
		350°C	550°C
1 : 1	50.00	26.0	16.0
1 : 2	33.50	23.0	15.4
1 : 3	25.00	21.0	14.4
1 : 4	20.00	20.0	14.0
1 : 8	11.11	18.6	13.0
1 : 16	5.80	17.0	12.0

*The effect of reaction temperature and space velocities on the activity of catalyst activated at 350°C:* The experiments were performed by varying the space velocities from 5000 h<sup>-1</sup> up to 12000 h<sup>-1</sup>. This series of experiments was carried out on the most active CuO/kaolin (1:1) at reaction temperatures 230, 280 and 320°C. The results of these experiments are listed in Table-2

TABLE-2  
EFFECT OF SPACE VELOCITIES ON THE ACTIVITY OF (1:1) CuO)/KAOLIN  
CALCINED AT 350°C (REACTION TEMPERATURES, 230, 280 AND 320°C)

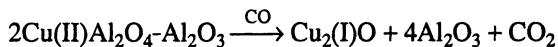
Space velocity h <sup>-1</sup>	% Conversion at reaction temperature		
	230°C	280°C	320°C
5000	30.0	40	60
9000	26.5	35	45
12000	20.0	30	40

The inspection of Table-2 revealed that the percentage of oxidation of carbon monoxide decreased with increasing the space velocity, *i.e.*, decreasing the contact time. Moreover, the increase of reaction temperature was accompanied by increasing the percentage of carbon monoxide oxidation. The space velocity 5000 h<sup>-1</sup> and the reaction temperature 320°C were found to be the optimum conditions for 1 : 1 CuO/kaolin catalyst calcined at 350°C.

*The state of Cu in the catalyst during catalysis:* Additional experiments were made to follow up the change of the state of copper in the catalyst. This was performed by heating the catalyst for about 20 h in a stream of air at 350 and 550°C. The produced solids were examined in CO-oxidation reaction. It was found that solids preheated for a long time showed the same activity as solids preheated at the same temperature for 4 h. X-ray analysis revealed that no change

in the structure of the two types of solids was detected. This indicates that heating for a long time did not change the activity or the structure of the solid catalyst; this is due to the absence of carbon monoxide with the excess oxygen used for activation.

In the present case the reduction of Cu(II) (existed in the octahedral vacancies) into Cu(I) (or CuO) which was accompanied by an increase in the cation radius<sup>6</sup> from 0.80 Å to 0.98 Å, leads to the destruction of the solid solution (CuAl<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>).



The formed Cu(I) or Cu(0) is immediately oxidized by oxygen into Cu(II) (CuO-phase)  $\text{Cu}_2\text{O or Cu} + \text{O}_2 \longrightarrow \text{CuO}$  and consequently the interaction between copper oxide with aluminum CuAl<sub>2</sub>O<sub>4</sub> (and not solid solution). The same process was also observed in case of the reaction of CuO with silica<sup>5</sup>. It was found that in the presence of oxidizing atmosphere, SiO<sub>2</sub> reacts faster with Cu<sub>2</sub>O than with CuO.

The above results are in agreement with those cited in literature. Jones and Taylor<sup>7</sup> were also found that carbon monoxide produces nuclei of metallic copper on cupric oxide (reduction of CuO). If oxygen was present in the carbon monoxide, it inhibited the reduction by oxidizing the copper nuclei as soon as they were formed.

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