

Effect of gamma-irradiation on surface and catalytic properties of CuO–ZnO/Al₂O₃ system

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A copper, zinc and aluminium mixed oxides sample having the nominal composition 0.25 CuO/0.03 ZnO/Al₂O₃ was prepared by impregnating Al(OH)₃ with copper and zinc nitrate solutions, drying at 100 °C then heating in air at 600 °C. The obtained solid was exposed to different doses of γ -rays (20–160 Mrad). The surface characteristics namely S_{BET} , V_p and r of different treated adsorbents were determined from N₂ adsorption isotherms measured at -196 °C. The catalytic activity of various irradiated solids was determined by following up the kinetics of CO-oxidation by O₂ at 150–200 °C. The results showed that the doses up to 80 Mrad resulted in no significant change in the S_{BET} but increased slightly the V_p (20%) of the treated adsorbents. The irradiation at 160 Mrad caused an increase of 20% in the S_{BET} of the irradiated solid sample. The catalytic activity increased progressively by increasing the dose, a dose of 160 Mrad brought about an increase of 140% in the catalyst's activity. The apparent activation energy of the catalytic reaction decreased monotonically by increasing the absorbed dose of γ -rays which was attributed to a parallel induced decrease in the value of pre-exponential term of the Arrhenius equation. The observed increase in the catalytic activity due to γ -irradiation has been interpreted as a result of increasing the concentration of catalytically-active sites contributing in chemisorption and catalysis of CO-oxidation via a possible fragmentation of CuO crystallites.

Introduction

Ionizing radiations have been reported to modify surface structural, textural, electric, and magnetic properties of a big variety of solids.^{1–9} Gamma-irradiation brought about a decrease in the surface area of graphite as a result of progressive blocking of pores as bulk expansion took place.¹ This treatment caused a significant increase in pore size of steam activated carbon due to possible radiolytic decomposition of oxygen complexes located on the carbon's surface.² Gamma-rays brought about a considerable decrease in the concentration of Brønsted acid sites of Na–Y zeolite and γ -Al₂O₃ due to progressive removal of OH groups on these solids.^{3,4} An increase in Lewis acid centers on Na–Y zeolite has been reported to take place by treatment with γ -rays.⁵ Gamma-irradiation increased the electrical conductivity of In₂O₃⁶ and decreased the effective paramagnetic moment of CuO loaded on Al₂O₃.⁷ It has been, also, reported that γ -rays led to removal of chemisorbed oxygen on unloaded Co₃O₄ solids and those loaded on γ -Al₂O₃.⁸ Gamma-rays effected a progressive decrease in both microstrain and lattice parameter of Co₃O₄ crystallites supported on γ -Al₂O₃⁹ due to removal of excess oxygen and fragmentation of its crystallites.

The effects of ionizing radiation on catalytic activities, in different reactions, made the object of several investigations.^{9–20} Gamma-rays enhanced the activity of ruthenium catalyst for methanation of CO and CO₂⁹ and increased the activity of H–Y zeolite for D₂–H₂ exchange reaction due to creation of skeletal lattice defects.⁴ Also, γ -irradiation of Pd, Pt–Pd and Rh

catalysts supported on Al₂O₃ much increased their catalytic activities in the hydrogenation of aromatic unsaturated compounds without changing the activation energies of the catalysed reactions.^{10–14} EL-SHOBAKY et al.^{15,16} reported that γ -irradiation much increased the catalytic activities of unloaded and γ -Al₂O₃ loaded Co₃O₄ solids in the catalysis of CO oxidation by O₂ without changing the activation energy of the catalysed reaction. It has been, also, reported that γ -rays enhanced the activity of CuO/Al₂O₃ towards the oxidation of CO with O₂.¹⁷ On the other hand, γ -irradiation of Fe₂O₃/Al₂O₃, unloaded NiO and CuO brought about a measurable decrease in their catalytic activities in CO-oxidation with O₂.^{18,19} Ionising radiations β , γ and fast neutrons effected an increase in the catalytic activity of low temperatures CO-conversion catalyst manufactured by BASF, K-3-10 (CuO–ZnO/Al₂O₃) in the following order β -rays > γ -rays > fast neutrons.²⁰

The induced changes in the catalytic activities of a big variety of catalysts due to exposure to different types of radiations might result from modifications in their surface, structural, textural, electric and magnetic properties. In most cases, the observed changes in the catalytic activities of different irradiated catalysts reflect corresponding changes in the concentration of the catalytically active sites.

The present work reports a study on the effects of different doses of γ -irradiation on surface and catalytic properties of CuO–ZnO/Al₂O₃ solids, using N₂ adsorption at -196 °C and catalysis of CO-oxidation of CO with O₂ at 150–200 °C over different treated solids.

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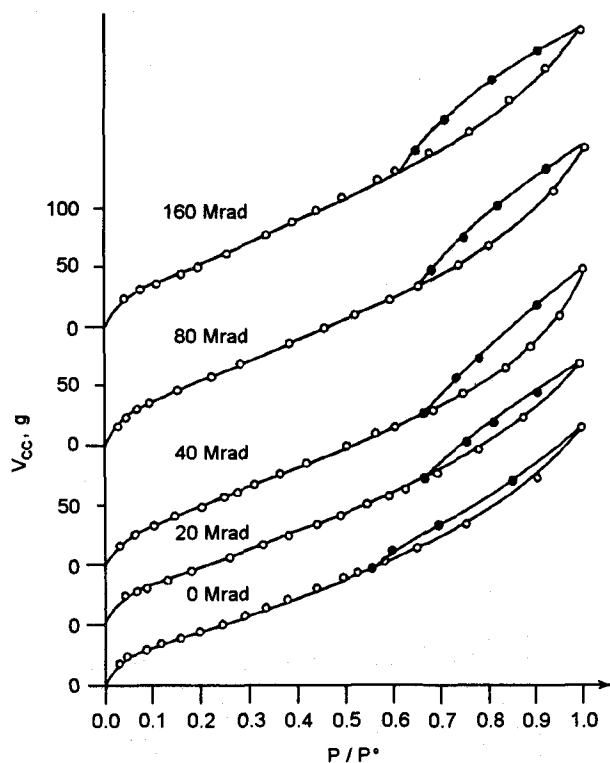


Fig. 1. N_2 -adsorption isotherms for different irradiated solids

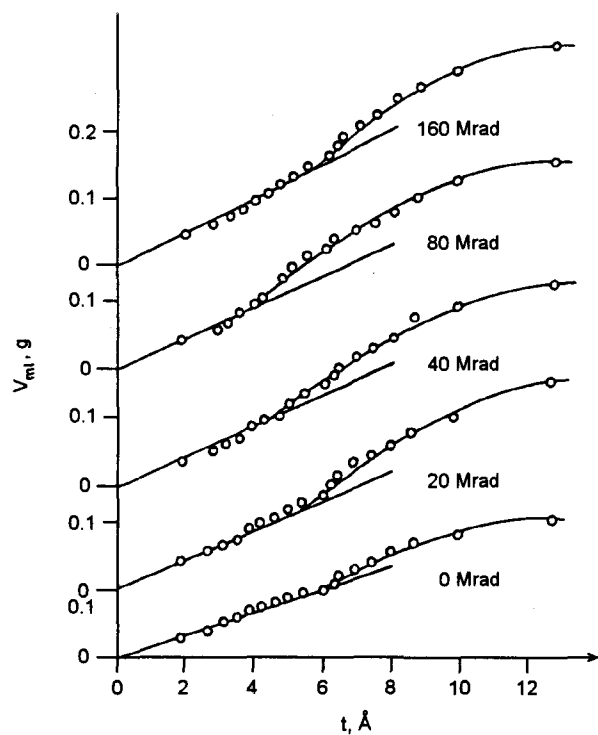


Fig. 2. Volume-thickness plots of various irradiated adsorbents

Experimental

Materials

A copper oxide supported on a poorly crystalline γ - Al_2O_3 pretreated ZnO was prepared by treating a known mass of $Al(OH)_3$ with a solution containing a calculated amounts of zinc nitrate, drying at $100^\circ C$ followed by calcination in air at $500^\circ C$ for 6 hours. The obtained solid was treated with copper nitrate solution dissolved in least amount of distilled water, drying at $100^\circ C$ and heating at $600^\circ C$ for 6 hours. The nominal composition of the prepared calcined solid sample was $0.25 CuO \cdot 0.03 ZnO \cdot Al_2O_3$. The employed $Al(OH)_3$ solid was prepared by precipitation from aluminium nitrate solution using $0.2M NH_4OH$ at $70^\circ C$ and pH 8, the precipitate was washed with distilled water and dried at $100^\circ C$ till constant weight. The chemicals employed were of analytical grade supplied by Prolabo Company.

Techniques

The X-ray diffraction patterns of the various irradiated samples were carried out using a Philips diffractometer (Type PW 1390). The patterns were run with nickel-filtered copper radiation ($\lambda = 1.5405 \text{ \AA}$) at 36 kV and 16 mA with a scanning speed of $2 \text{ deg in } 2\theta \cdot \text{min}^{-1}$.

The surface properties, namely S_{BET} , V_P and r of various adsorbents were determined from N_2 adsorption isotherm at $-196^\circ C$ using a conventional volumetric apparatus. Before carrying out the measurements each sample was degassed under a reduced pressure of 10^{-6} torr at $200^\circ C$ for 3 hours.

The catalytic oxidation of CO with O_2 on different catalysts was carried out at various temperatures 150 – $200^\circ C$ using a static method. A stoichiometric mixture of CO and O_2 at a pressure of 2 torr was used. A fresh 200 mg catalyst – sample was employed for each kinetic experiment and was activated by heating at $300^\circ C$ for 2 hours under a reduced pressure of 10^{-6} torr. The kinetics of catalyzed reaction were followed up by measuring the pressure of the reaction mixture at different time intervals till equilibrium was attained. The reaction product (CO_2) was removed from the reaction atmosphere by freezing in a liquid nitrogen trap, so the percent drop in pressure of the reaction mixture at a given time interval gives the percent conversion of the catalytic reaction at that time.

The prepared catalyst sample, preheated at $600^\circ C$, was exposed to different doses of γ -irradiation using a ^{60}Co source. The doses were 20, 40, 80 and 160 Mrad at rate of $27 \text{ rad} \cdot \text{s}^{-1}$. The irradiated catalysts samples were left 2 weeks before the different measurements were carried out.

Table 1. Some surface characteristics of the irradiated solids preheated in air at 600 °C

Dose, Mrad	S_{BET} , m ² /g	S_p , m ² /g	V_p , cm ³ /g	r , Å	C-BET constant
0	190	210	0.285	28	16
20	185	210	0.304	33	26
40	208	220	0.322	31	21
80	208	230	0.338	32	21
160	237	250	0.341	29	15

Results and discussion

Effect of γ -irradiation on surface properties of various adsorbents

CuO-ZnO/Al₂O₃ solid specimens were exposed to different doses of γ -irradiation, namely 20, 40, 80 and 160 Mrad. The different surface characteristic of these solids were determined from N₂ adsorption isotherms conducted at -196 °C. These isotherms belong to type II of Brunauer classification.²¹ The obtained isotherms are given in Fig. 1.

The specific surface areas S_{BET} of various adsorbents were computed from the linear plots of the BET equation. The data of S_{BET} obtained are given in Table 1. Also included in Table 1 are the total pore volume V_p and mean pore radius r .^{22,23}

An additional set of surface areas S_p was obtained from volume thickness curves (V_{1-t} plots). The obtained V_{1-t} plots (Fig. 2) are similar to each other for the various irradiated adsorbents. These plots are constructed using suitable standard t -curves²³ depending on the magnitude of the C constant in the BET equation. The calculated values of S_p are also included in Table 1. It is seen from Fig. 2 that all adsorbents employed consisted, mainly, of wide pores as indicated from their upward deviation. Inspection of Table 1 shows that (1) the values of S_{BET} and S_p are close to each other which reflects the correct choice of the reference t -curves for analysis and shows the absence of ultramicropores in the investigated adsorbents, and (2) γ -irradiation at doses up to 80 Mrad exerted no significant changes in the specific surface areas of the treated solids, a dose of 160 Mrad, however, resulted in an increase of 25% in the S_{BET} . This treatment (40–160 Mrad) brought about an increase of about 20% in the V_p of the irradiated catalysts. The observed increase in both S_{BET} and V_p due to γ -irradiation could not be related to possible changes in the pore size of the treated adsorbents which exhibited similar values of mean pore radius r . The highest dose of γ -irradiation, 160 Mrad, might result in fragmentation of the catalyst's crystallites leading to an increase of its specific surface area.

Effect of γ -irradiation on the catalytic activity of different solids

The catalytic oxidation of CO by O₂ on various irradiated catalysts was performed at 150, 175 and 200 °C.

The results showed that the catalytic reaction followed first-order kinetics (Fig. 3). Representative kinetic curves and first-order plots are dose in the range of 20–80 Mrad, irradiation at a dose of 160 Mrad, although, brought about a further increase in the value of k , k remained almost unchanged (Fig. 4). The induced increase in the catalytic activity, and the catalytic per unit area for the reaction conducted at 175 °C due to irradiation at 160 Mrad are 160 and 120%, respectively. The significant increase in the catalytic activity due to γ -irradiation could not be attributed to induced increase in the specific surface areas of the treated solids simply because the catalytic activity per unit area was considered. It has been reported that the exposure of Co₃O₄/Al₂O₃ and CuO/Al₂O₃ solids to γ -rays resulted in increasing their catalytic activities in CO-oxidation by O₂.^{15,17} However, the unloaded NiO and CuO catalysts

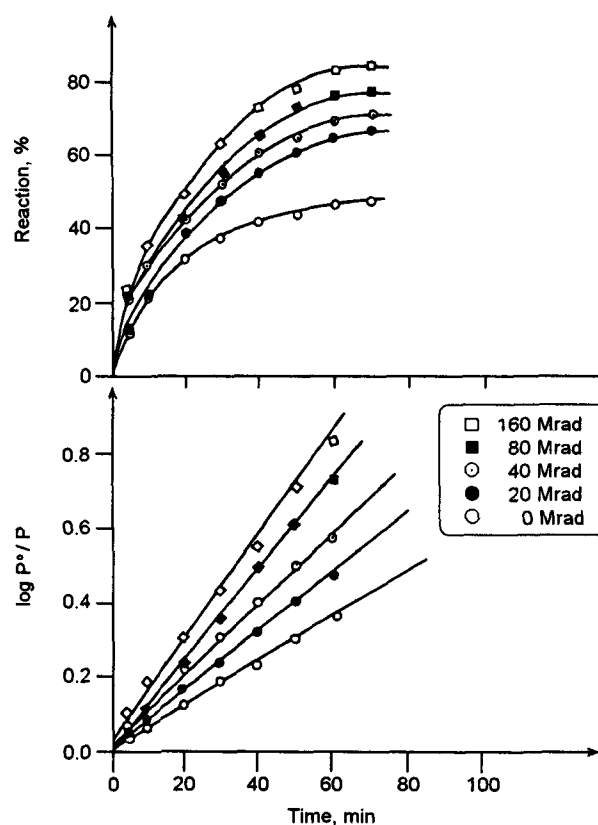


Fig. 3. Kinetic curves and first order-plots of CO-oxidation by O₂ at 175 °C over γ -irradiated catalysts

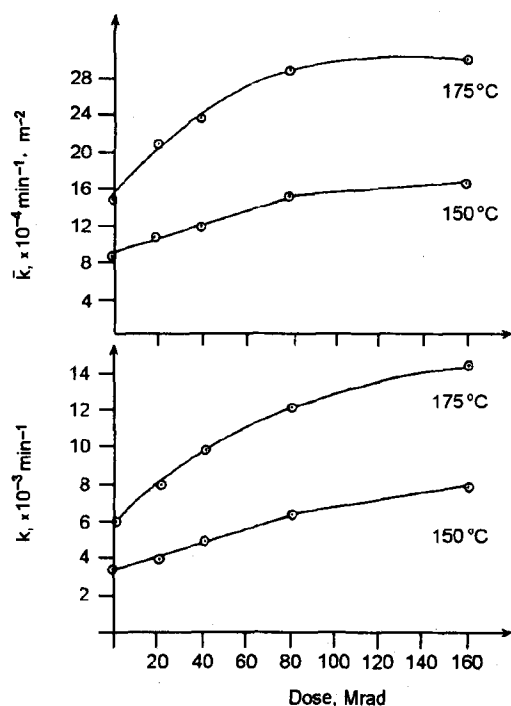


Fig. 4. Variation of reaction rate constant k and reaction rate constant per unit surface area \bar{k} for CO-oxidation by O_2 at 150 and 175 °C as a function of the dose of γ -rays

showed a significant decrease in their catalytic activities, in CO oxidation by O_2 , when being treated with γ -rays. These results and those found in the present work showed the role of metal-support interactions in modifying the catalytic activities of various supported catalysts due to treating with γ -rays. In other words, one can suggest that γ -rays might modify the metal support interactions leading to the formation of the corresponding aluminate besides the removal of surface hydroxyl groups that might be present on the catalyst's surface.¹⁷ The transformation of some of metal oxide into the corresponding aluminate might be followed by a decrease in the catalytic activity of the treated solids.²⁴ On the other hand, the removal of surface OH groups might result in an increase in the activity of the irradiated catalysts.¹⁷ In fact, OH groups do not contribute directly in oxidation-reduction reactions and block some surface sites, their removal might liberate these sites which became susceptible for chemisorption and catalysis of oxidation-reduction reactions. The investigated CuO/ZnO/Al₂O₃ catalyst being heated at 600 °C did not contain any OH groups on its surface.¹⁵ So, the effect of γ -irradiation on metal support interactions must be regarded as an important factor in changing the catalytic activity of the irradiated catalysts. Moreover, γ -rays might also lead to fragmentation of crystallites of the irradiated solids.⁸ This process is normally accompanied by an increase in the concentration of catalytically active sites and hence a corresponding increase in the activity of the

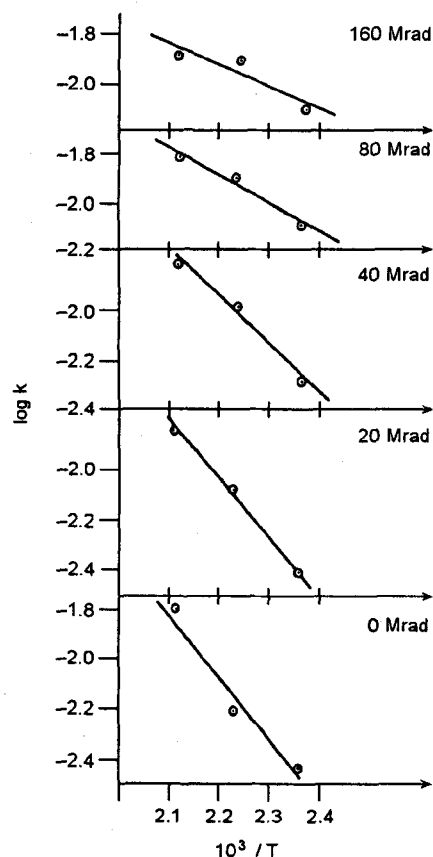


Fig. 5. Arrhenius plots of CO-oxidation reaction conducted over the various irradiated catalysts at temperatures between 150–200 °C

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The determination of the activation energy (ΔE) of CO-oxidation by O_2 on various irradiated catalysts might throw some light about the role of γ -rays on modifying the mechanism of the catalysis of CO-oxidation

Table 2. Apparent activation energies ΔE and ΔE^* and frequency factor (A) of catalytic oxidation of CO over irradiated catalyst specimens

Dose, Mrad	ΔE (150–200 °C), kJ · mol ⁻¹	log A	ΔE^* (150–200 °C), kJ · mol ⁻¹
0	47.9	3.40	47.9
20	45.9	3.22	47.4
40	37.6	2.34	46.7
80	22.0	0.63	46.0
160	17.7	0.08	46.3

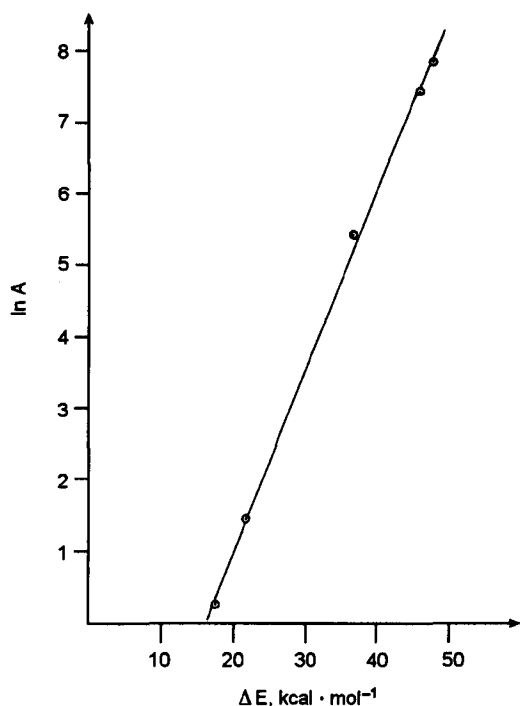


Fig. 6. Relationship between ΔE and frequency factor $\ln A$ for the catalytic reaction conducted over different irradiated catalysts

by O_2 . Figure 5 shows the Arrhenius plots of CO oxidation by O_2 at 150–200 °C over the various irradiated catalysts. The computed ΔE values are given in Table 2. It is clear

from Table 2 that γ -irradiation brought about a progressive decrease in the value of ΔE which decreased from 45.9 to 17.7 $\text{kJ} \cdot \text{mol}^{-1}$ by increasing the dose from 20 to 160 Mrad. These results reflect clearly the observed increase in the catalytic activities of the irradiated catalysts. Table 2 includes also the values of the pre-exponential factor of the Arrhenius equation (A). The computed values of A factor are also given in Table 2. It is seen from Table 2 that γ -irradiation led to a progressive decrease in the value of A parameter which may be an indication of the heterogeneity of the catalyst's surface. The activation energy of the catalysis of CO-oxidation by O_2 was recalculated adopting the A value of the non-irradiated catalyst specimen for the other irradiated catalysts and the obtained ΔE^* values are given in the last column of Table 2. The ΔE^* values are almost the same for the different irradiated catalysts ($47 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$). These results show that γ -irradiation did not change the mechanism of the catalytic reaction but increased the concentration of the catalytically-active sites in the irradiated solids. This conclusion finds an additional evidence from the plot of the equation $A = a \cdot \exp h\Delta E$ derived on the basis of the dissipation function of active sites by their energy as a consequence of surface heterogeneity: $F(E_i) = a \cdot \exp hE_i$ where E_i is the energy of interaction of site i with the substrate.²⁵ The plot of $\ln A$ versus ΔE for different irradiated catalyst samples gives a straight line (Fig. 6) its slope and intercept determines the values of h and a , respectively. The computed values of the constants h and a are 0.25 and 0.67, respectively. The constant h and a values indicate that the irradiation does

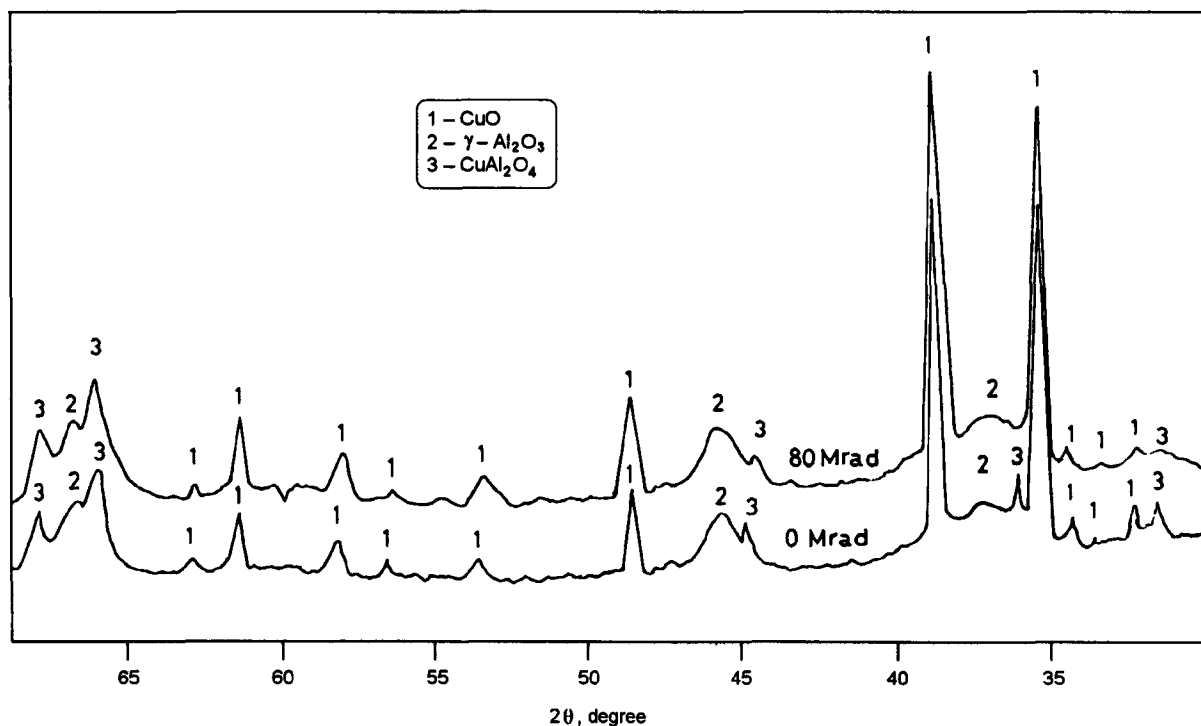


Fig. 7. X-ray diffractograms of unirradiated and γ -irradiated catalyst samples preheated at 600 °C

not change the dissipation of the active sites, i.e., the character of the surface heterogeneity. In other words, γ -rays does not change the energetic nature of the active sites, but changes (increases) their concentration.

Effect of γ -irradiation on metal support interactions

The metal support interaction occurring in the investigated CuO–ZnO/Al₂O₃ system leading to the formation of copper aluminate was studied via XRD analysis. Figure 7 shows X-rays diffractograms of the un-irradiated and γ -irradiated catalysts preheated at 600 °C. It is seen from Fig. 7 that the investigated solids consisted of CuO as a major phase together with a poorly crystalline γ -Al₂O₃ and CuAl₂O₄ phases. Inspection of Fig. 7 reveals that γ -irradiation at a dose of 80 Mrad brought about a slight decrease in the intensity of the diffraction lines of CuO phase and a small increase in the intensity of the diffraction lines of CuAl₂O₄ phase. These findings might indicate that γ -rays resulted in fragmentation of some of CuO crystallites, this process might be followed by a slight decrease in the crystallinity of CuO phase. The observed increase in the intensity of the diffraction lines of CuAl₂O₄ phase due to γ -irradiation might reflect an increase in its amount present. In other words, γ -irradiation enhanced the formation of CuAl₂O₄. The aluminate produced showed a catalytic activity smaller than that of CuO²⁴ and γ -irradiation might result in a decrease in the activity of treated solids. This speculation has not been verified since an increase in the activity of irradiated catalysts was found. The observed increase in the catalytic activity of CuO–ZnO/Al₂O₃ solids due to γ -irradiation might be due to a significant increase in the concentration of catalytically active sites via fragmentation of copper oxide crystallites.

Conclusions

These are the main conclusions that can be derived from the results obtained:

(1) Gamma-irradiation at doses up to 80 Mrad resulted in no significant change in the S_{BET} areas of the treated solids, however, a dose of 160 Mrad, exerted an increase of about 25% in the S_{BET} and V_p of the irradiated adsorbent.

(2) The catalytic activity, in CO-oxidation by O₂, of the various irradiated solids increased progressively by increasing the dose in the range 20–160 Mrad. An increase of 160% in the catalytic activity was attained by exposure to a dose of 160 Mrad.

(3) The apparent activation energy of the catalysis of CO-oxidation by O₂ over different irradiated catalysts decreased monotonically as a function of the dose of

γ -rays. This decrease was attributed to a parallel decrease in the magnitude of pre-exponential factor of the Arrhenius equation (A). Almost the same values of the activation energy have been found by adopting the A value of the un-irradiated solid to the other irradiated catalysts. This indicates that γ -rays did not modify the mechanism of the catalytic reaction but resulted in a progressive increase in the concentration of the catalytically-active species via fragmentation of CuO crystallites.

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