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Investigating the Effect of CuO/NiO and CuO/CoO Relative Composition on the Reduction Time of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ with Methane Gas as the Reducing Agent in the Synthesis of Nano-bimetallic Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$

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Abstract

In this paper, the reduction duration of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ binary mixtures was studied using thermogravimetric method. The reduction reaction was performed using copper, nickel and cobalt oxides as metal precursors and methane gas as the reducing agent, under atmospheric pressure. The products as well as the raw materials were characterized and analyzed using X-Ray diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). Initially, CoO, NiO and CuO were transformed to Co, Ni and Cu through reduction reactions with 23 Vol.% of methane at 830 °C. Results demonstrated that the reduction times of NiO, CoO and CuO NPs with CH_4 at 830 °C were 14, 39 and 47 min, respectively. EDS and XRD analysis indicated that more than 97 % of copper, nickel and cobalt oxides were transformed to copper, nickel and cobalt NPs. The reaction time of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ binary mixtures with methane was investigated to evaluate the effect of CuO (x=0, 0.4, 0.6, 1) relative composition. In addition, the reaction time of ternary mixture of $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ with methane gas was also studied.

Keywords

binary metal, Cu-Ni, Cu-Co, methane, the reduction time, thermogravimetric method

1 Introduction

In recent years, the synthesis of metallic Nanoparticles (NPs) and their mixtures in comparison to micro-structured materials have attracted many researchers due to their unique features including fine particle sizes and high surface to volume ratio [1, 2]. Among metallic nanoparticles, copper, nickel, cobalt and their binary and ternary mixtures possess great significance in various industrial applications which stem from their outstanding physical and chemical properties. In this regard, unique electrical, catalytic and thermal characteristics along with high surface to volume ratio, resistance to corrosion, great flexibility and strength are considered as their main features [3-6].

Copper-nickel and copper-cobalt binary nanoparticles (BNPs) are consisted of copper and nickel and cobalt and copper metals, respectively, which provide many applications in different fields, compared to single-metal copper, nickel and cobalt nanoparticles, due to the composition of different percentages, varied particle sizes and the coexistent properties of both metals (copper and nickel or copper and cobalt) [7-11]. Nickel is completely mixed with copper and the resulting alloy only contains one phase in any ratio. The most important property of nickel-copper alloy is the variation in the thermal expansion of the alloy with the amount of nickel, making it possible to make alloys with defined and precise thermal expansion. The presence of nickel in copper-nickel alloy increases the hardness which maintains even at high temperatures [12-14].

Cu-Ni and Cu-Co BNPs not only possess the combined properties associated with the presence of both copper and nickel and copper and cobalt in the mixture, but also it is expected that this composition can induce new chemical, biological, mechanical, and thermal properties, due to the correlation between the metals in the binary mixture. Binary nanoparticles (BNPs) are generally nano-sized multi-purpose materials which are used in various applications. In fact, application of these materials can

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increase the activity and stability of the catalyst, reduce the formation of carbon in the reaction of dry methane reforming, increase the strength of super alloys and fix the shape and sizes of the particles [15-19].

Different methods are commonly applied for the synthesis of mono-metal NPs (copper, nickel and cobalt) and copper-nickel and copper-cobalt binary mixtures including photolytic reduction, electrodeposition, uranium purification, electrolytic plating, thermal plasma synthesis, and microwave-hydrothermal [3, 9, 20-24].

Along with the benefits of synthesizing Cu-Ni and Cu-Co bimetallic (BM) with conventional methods, important negative points also exist, including excessive number of steps, long synthesis time, high amounts of precursors required in the synthesis, challenging control over several simultaneously effective parameters in the production of Cu-Ni and Cu-Co BM with appropriate particle size and shape [5, 25-30]. The choice of a suitable method for the synthesis of Cu-Ni, Cu-Co BM, according to which it could be possible to select the relative composition of Ni and Co in $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ and control the effective parameters to produce CuNi and CuCo BM with desired properties, is considered an important issue for many researchers.

The aim of the present study is to investigate the duration of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ reduction reaction with methane for the synthesis of Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ with thermogravimetric(TG) method. The production of metals from metal oxides using reduction reactions using of methane gas reducing agent is much cleaner and more cost-effective than conventional methods. Synthesis of binary nano-metal mixture from powdered metal oxide NPs with TG method reduces the number of synthesis steps, increases the selectivity over shape and size of the particles and simplifies accurate control of the composition of each metal (copper, nickel and cobalt) in Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$.

2 Experimental section

2.1 Materials

Nickel oxide (NiO), copper oxide (CuO) and cobalt oxide (Co_3O_4) powder NPs (Beckman Coulter Commercial Enterprise, China) were used in all experiments in order to evaluate the reduction time of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$.

2.2 Thermogravimetric method

In this study, binary mixture of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ was applied to investigate the reduction time and synthesis of Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BM using TG method. "x" represents relative weight percentage of copper oxide and copper (x= 0, 0.4, 0.6, 1) in raw materials and products. A mixture of metal oxides was carried out using Ball-mill (Model: NARYA-BM 25). The mixing time is about 25 minutes. According to this method, methane is used as the reducing agent to transform $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ mixtures to Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BM. The reduction reaction of CuO, NiO and CoO with methane gas is as follows [6, 31, 32]:

$$4CuO(solid) + CH_4(gas) \rightarrow 4Cu(solid) + CO_2(gas) + 2H_2O(gas) \tag{1}$$

$$NiO(solid) + CH_4(gas) \rightarrow Ni(solid) + CO(gas) + 2H_2(gas) \tag{2}$$

$$CoO(solid) + CH_4(gas) \rightarrow Co(solid) + CO(gas) + 2H_2(gas) \tag{3}$$

Fig. 1 illustrates the schematic diagram of the experimental setup used for the preparation of Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BNPs with methane gas. In TG method, pellets of the raw oxide particles with average diameter of 10.30 mm and average thickness of 3mm (±0.3mm) were prepared (pressed under 195 bar). The prepared pellets were transferred into a suspended basket under the balance (RADWAG-As310 R2 with precision of ±0.0001) which was connected to a computer and recorded the weight changes every 10 seconds.

Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BM were prepared from the reduction of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ at constant temperature of 830ºC and atmospheric pressure. The $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ pellets with varied weight percentage of copper oxide (x=0, 0.4, 0.6, 1) were placed in a quartz reactor (diameter of 4 cm and length of 58 cm) embedded within a vertical furnace. As the temperature was stabilized (at reaction temperature of 830 °C), the reduction of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ mixtures initiated using argon and methane gas. A mixture of methane and argon gas with flow rate of 296 cc/min and 23 Vol.% of methane was used through the reduction reactions. Argon gas was applied before the temperature increase (to the reduction temperature) and in the cooling section (reduction of to room temperature after the reduction reaction). A mixing chamber comprised of ceramic balls was inserted before the entrance of the reactor (in the lower part of the reactor (5 cm)) in order to thoroughly mix methane and argon gases.

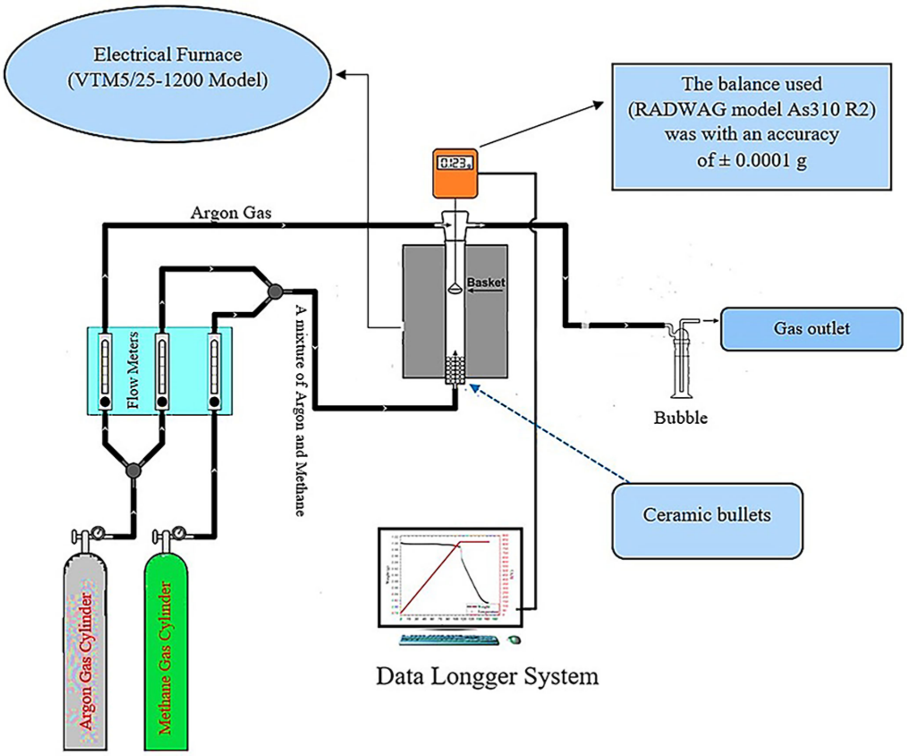

Fig. 1 The schematic of the experimental setup to evaluate the reduction time of binary and ternary metal oxide mixtures.

2.3 Material characterization

The as-prepared samples were characterized by X-ray powder diffraction (XRD, D8, Bruker) using Cu Kα radiation with graphite monochromator in a 2θ range of 10° to 90°. The average sizes of Cu, Ni and Co NPs were estimated using the Scherrer Eq. (4) [24, 33, 34]. The Scherrer Eq. (4) is as follows:

$$D_P = \frac{K \times \lambda}{\beta \times \cos\theta} \tag{4}$$

In which, D_p is the average size of the particles, K is the shape factor (0.89), λ is the X-ray wavelength, θ is the angle of reflection and β is the full width half maximum (FWHM) in radians [33, 35].

EDS analysis was utilized to determine the chemical composition and purity of Cu, Ni and Co NPs in samples recovered by methane gas.

3 Results

3.1 Characterization of raw materials

The XRD patterns of NiO, CuO and Co_3O_4 metal oxides which were used to synthesize different mono-, binary- and ternary NPs are depicted in Fig. 2.

The average particle sizes of raw NiO, Co_3O_4 and CuO, calculated from XRD analysis and Eq. (4), were 33.71, 35 and 34.25 nm, respectively. In the XRD pattern of raw samples, the peaks associated with nickel, cobalt and copper oxides were only observed.

3.2 Experimental results

The reaction of $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ mixtures with 23 Vol.% of methane at 830 °C for the preparation of Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BM was investigated

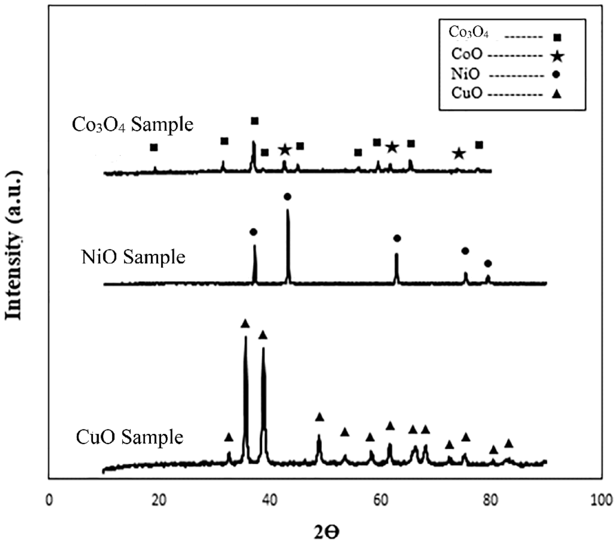

Fig. 2 XRD analysis of raw samples of NiO, Co_3O_4 and CuO.

[6, 31, 32, 36]. Process conditions such as reaction temperature and volume percentage of methane gas were considered the same for all the samples in order to compare the results more precisely. Ni-Cu and Cu-Co BM were produced with different relative compositions after the reaction. The weight loss curve in Fig. 3 indicates the successful reduction reaction of CuO, NiO, Co_3O_4, $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ with methane reducing gas and production of Ni_x-$Cu_{(1-x)}$ and Cu_x-$Co_{(1-x)}$ BM with TG method.

The experimental results in Fig. 3 demonstrate that, as the temperature was stabilized (at 830 °C), Co_3O_4-containing samples encountered a weight loss in the presence of argon through which Co_3O_4 converted to CoO, even before the reduction reaction with methane gas was initiated [6]. The conversion time of Co_3O_4 to CoO was found to be different depending on the amount of Co_3O_4 in the samples. For instance, in the samples with 100% Co_3O_4 sample, the conversion of Co_3O_4 to CoO took about 44 min (Fig. 3c) while it took only 28 min for samples containing 60 wt.% of Co_3O_4 (Fig. 3e). In addition, in the ternary $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ mixture, containing 20 wt.% of Co_3O_4, Co_3O_4 conversion to CoO was about 15 min (Fig. 3f).

The conversion–time curves can be obtained from the TG data by using the following relationship[1, 2]:

$$X(t) = \frac{W_0 - W(t)}{W_0 \dfrac{M_O}{M_w}} \tag{5}$$

Where W(t) is the measured weight at time t, W_0 denotes the initial pellet weight, and M_O and M_w ($M_W = \sum W_i M_i$ i= $(CuO)_x$-$(NiO)_{(1-x)}$ and (CuO)$_x$- $(Co_3O_4)_{(1-x)}$ (x=0, 0.4, 0.6, 1)) represent the molecular weights of released oxygen and metal oxide NPs, respectively.

In this study, the reduction time of copper, nickel and cobalt oxide was investigated. TG results were confirmed by XRD and EDS analyzes, therefore, only TG results corresponding to the reduction time of $(CuO)_x$-$(NiO)_{(1-x)}$ and (CuO)$_x$- $(Co_3O_4)_{(1-x)}$ mixture was further used.

Fig. 4 illustrates the conversion rates of NiO, CuO and CoO to Ni, Cu and Co NPs at 830 °C. As can be seen, the reduction time of NiO, CoO and CuO NPs with CH_4 at 830 °C were 14, 39 and 47 min, respectively.

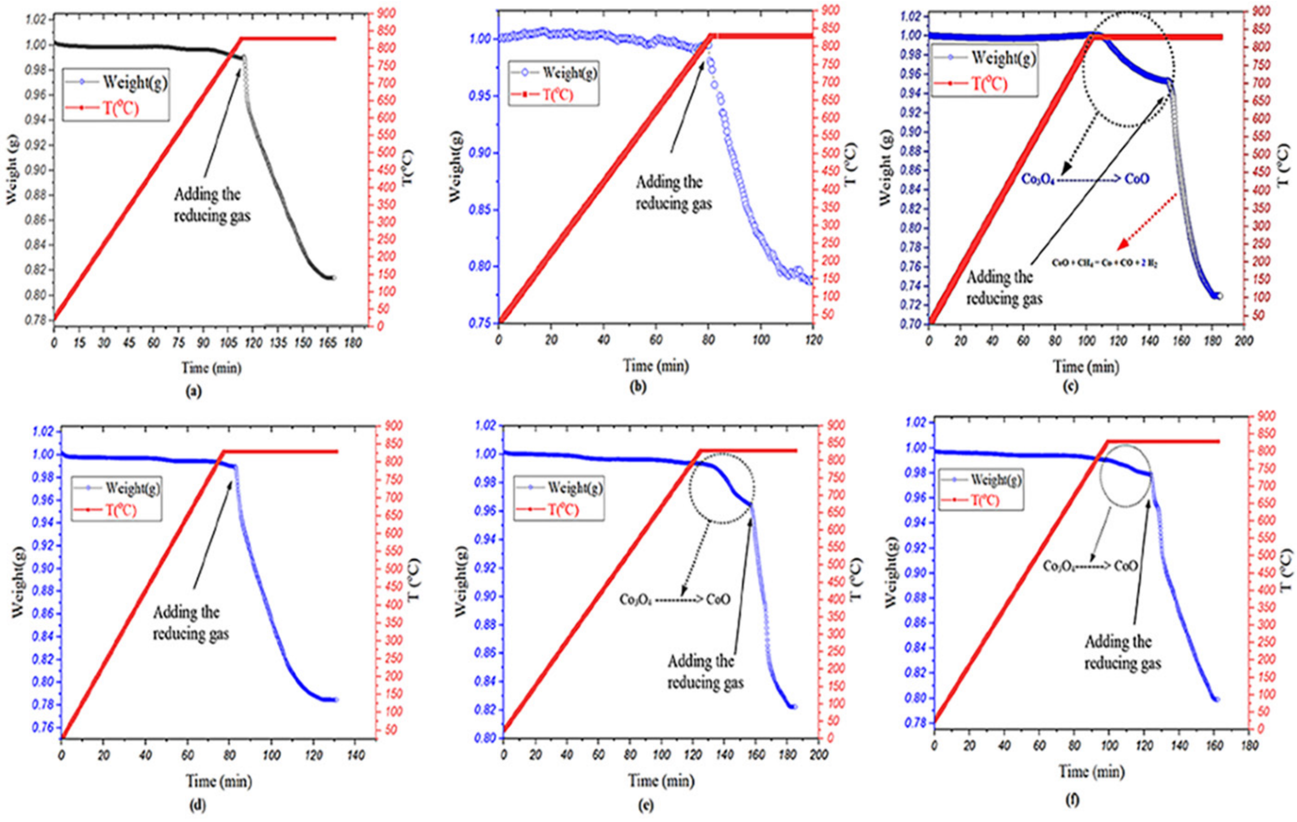

Fig. 3 The weight loss curve of (a) pure copper, (b) pure nickel, (c) pure cobalt, (d) binary $(CuO)_x$-$(NiO)_{(1-x)}$, (e) binary $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ and (f) ternary $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ at 830 °C

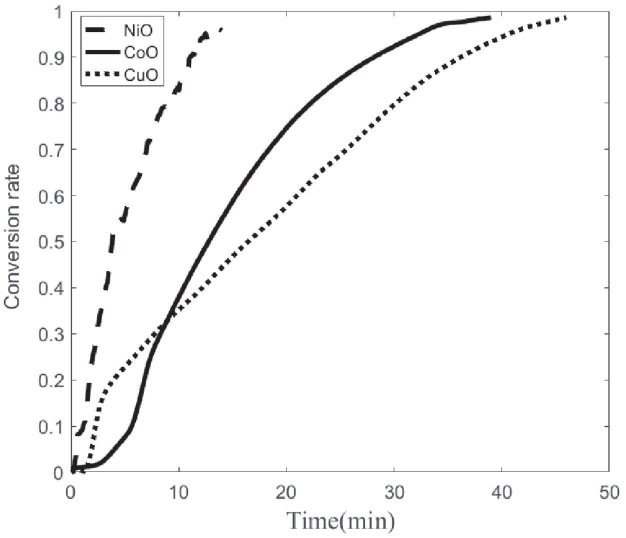

Fig. 4 The conversion rates of NiO, CoO and CuO to Ni, Co and Cu NPs.

3.2.1 Structural features of synthesized Cu, Ni and Co NPs

Fig. 5 indicates XRD patterns of Cu, Ni and Co NPs which were produced at 830 °C with 23 Vol.% of methane. The XRD results clearly indicates that CuO, NiO and Co_3O_4 completely transformed to Cu, Ni and Co metal NPs. The average particle sizes of Cu, Ni and Co which were calculated from Eq. (4) were 46, 32.71 and 22.78 nm, respectively.

The purity evaluation of the synthesized Cu, Ni and Co NPs at 830 °C were performed using EDS analysis which are indicated in Fig. 6. It was revealed that more than 97-98 % Cu, Ni and Co NPs were produced. The EDS results are highly in consistence with the obtained results from TG method.

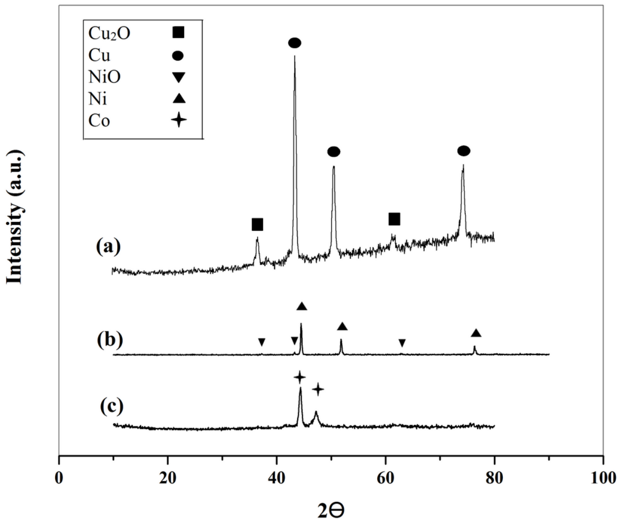

Fig. 5 XRD analysis of (a) Cu, (b) Ni and (c) Co products.

3.2.2 Effect of CuO/NiO ratio on the reduction reaction of $(CuO)_x$-$(NiO)_{(1-x)}$

$(CuO)_x$-$(NiO)_{(1-x)}$ was produced with different weight composition (x=0, 0.4, 0.6, 1) from the reduction of their corresponding metal oxides using methane gas. It is evident in Fig. 7 that, for all the samples in the initial minutes, the reaction of the solid pellet reagent with methane is rapid and therefore the conversion gradient is sharp, however, over time, the product layer is formed around the surface of the pellet, which reacts with solid reagents and also responds slowly due to the decrease in the amount of oxygen [37, 38]. As a result, the slope of the change in conversion rate decreases with time. For instance, for CuO, in the first 10 minutes, the gradient is steep, but as time passes, the product layer of Cu NPs is formed around the surface of the pellet, which causes the porosity blockage in the reactive solid, and also due to the reduction in the amount of oxygen, the reaction speed is restored. As a result, the slope of the conversion rate decreases with time, which is about 37 minutes in which diffusion through the product layer is the rate controlling phenomena.

In addition, results indicated that the reduction time of $(CuO)_x$- $(NiO)_{(1-x)}$ mixture is dependent on the weight percentage of CuO in the mixture; increased amount of CuO diminishes the reduction reaction. In this regard, the reduction of $(CuO)_{0.4}$ -$(NiO)_{0.6}$ and $(CuO)_{0.6}$-$(NiO)_{0.4}$, was carried out within 28 and 35 minutes, respectively (Fig. 7).

3.2.3 Effect of CuO/CoO ratio on the reduction reaction of $(CuO)_x$-$(Co_3O_4)_{(1-x)}$

$(CuO)_x$-$(Co_3O_4)_{(1-x)}$ with varied relative weight compositions was prepared from their metal oxide reduction using methane. The results represented in Fig. 8 indicate that the reduction of $(CuO)_{0.4}$-$(Co_3O_4)_{0.6}$ and $(CuO)_{0.6}$-$(Co_3O_4)_{0.4}$ took 39 and 42 min, respectively. The conversion reactions of copper oxide, in +2 to 0 oxidation states, is as follows [39]:

$$CuO \rightarrow Cu_4O_3 \rightarrow Cu_2O \rightarrow Cu \qquad (6)$$

It is also observed that the slope of $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ conversion rate in the reduction reaction is less than pure CuO and Co_3O_4. This can be attributed to the rapid movement of copper oxide ions on the surface of the pellet at high temperature as Co_3O_4 is being transformed to CoO, even before the reduction reaction. As well as, it is probably due to the presence of two layers of metal oxides at high temperature (830 °C) [40, 41]. The inner layer is only Cu_2O+CoO and the outer layer is made of CuO+Cu_2O+CoO mixture.

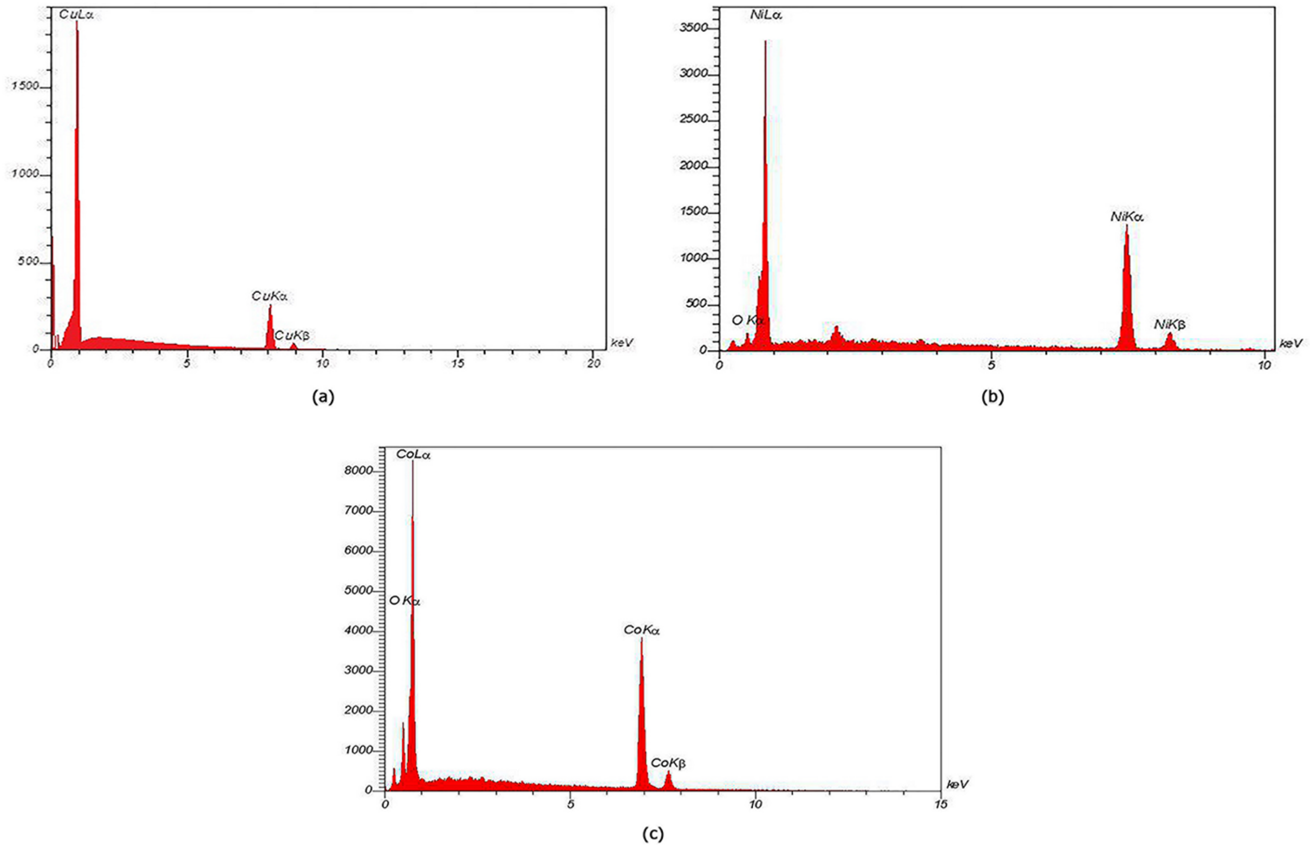

Fig. 6 EDS analysis of Mono-NPs at 830 °C: (a) Cu, (b) Ni and (c) Co.

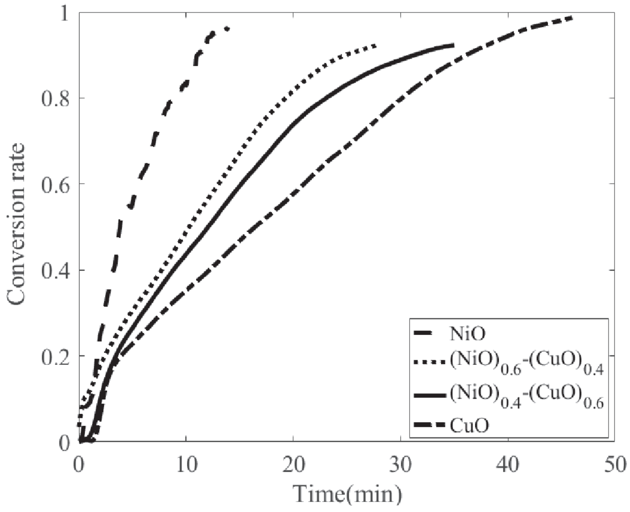

Fig. 7 Effect of CuO/NiO ratio on the conversion rate and the duration of the reduction reaction at 830 °C.

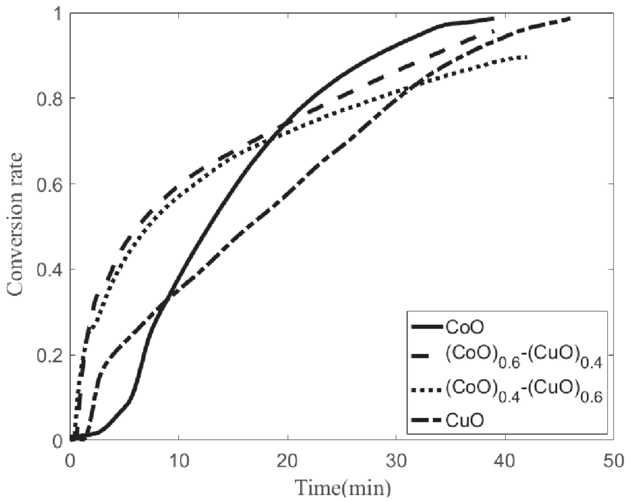

Fig. 8 Effect of CuO/Co_3O_4 ratio on the conversion rate and the duration of the reduction reaction at 830 °C.

Fig. 9 indicates XRD patterns of $(CuO)_{0.4}$ -$(NiO)_{0.6}$ and $(CuO)_{0.4}$-$(Co_3O_4)_{0.6}$ which were reduced at 830 °C with 23 Vol.% of methane. As can be seen in Fig. 9. in both samples, a very small amount of unreacted metal oxide (NiO, CuO and CoO) remained. This can be attributed to the formation of bimetallic layer around the pellet and decreasing the methane diffusion into the core of the pellet due to the thickness of the pellet [38].

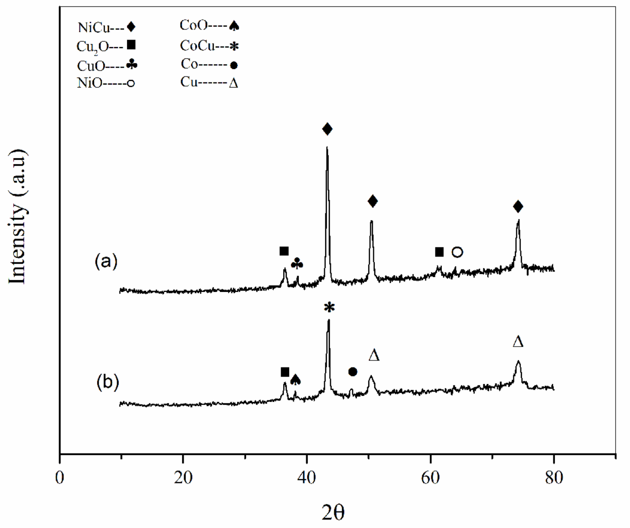

Fig. 9 XRD analysis of (a) and (b) are $(Cu)_{0.4}$ -$(Ni)_{0.6}$ and $(Cu)_{0.4}$-$(Co)_{0.6}$ respectively.

3.2.4 Reduction reaction of $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ with methane

Fig. 10 shows the conversion of $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ ternary mixture to $Ni_{0.6}$-$Cu_{0.2}$-$Co_{0.2}$ compared to their corresponding pure state conversion with time. Based on the results, the duration of $(NiO)_{0.6}$-$(CuO)_{0.2}$-$(Co_3O_4)_{0.2}$ reduction with methane and its conversion to $Ni_{0.6}$-$Cu_{0.2}$-$Co_{0.2}$ was 22 min.

Comparison of nickel oxide conversion curves and its reduction with methane with other reduction curves, reveals a significant difference, which can be assigned to the fact that in all the reduction reactions, the progression of the reaction usually reduces the speed of the reaction, however, in this case the rate does not decrease with the advancement of the reaction, and even in the final reaction times, the curve still continues to grow. This can be assigned to the autocatalysis effect of nickel atoms formed as a result of the reduction reaction, which ultimately increases the reaction speed [42]. As the reaction proceeds, the concentration of nickel (catalyst) also increases which intensifies its effect on the reaction rate [32, 43]. This is in contrast with the behavior of all CuO-containing samples, in which the reaction rate is initially high and further decreases as the reaction progresses. Copper oxide seems to act as a promoter in the ternary mixtures. In addition, another factor which is responsible for the decrease in the speed of the recovery reaction for CuO-containing samples is the rapid sintering of Cu particles according to its thermal properties relative to Ni and Co [19, 44, 45]. Thermal properties are presented in Table 1.

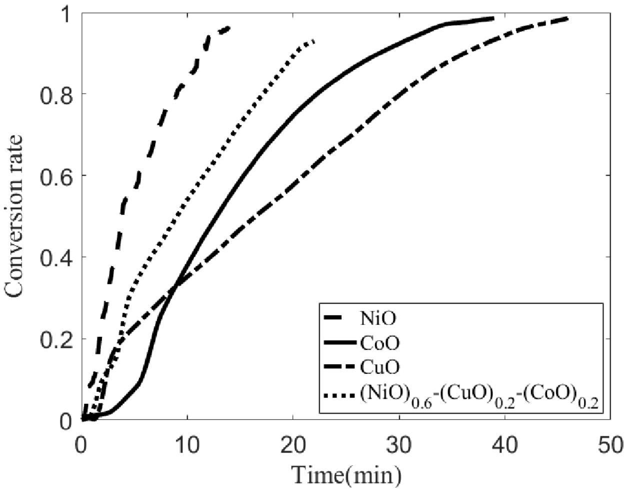

Fig. 10 Comparison of conversion rates for ternary mixture and mono-metal oxide samples.

Table 1 Thermal Properties

	Co	Ni	Cu
Melting Point (T [=]°C)	1495	1455	1084.62
Heat of Fusion (kJ/mole)	16.2	17.2	13.1

4 Conclusions

Copper, nickel and cobalt nanoparticles (NPs) along with binary copper-nickel and copper-cobalt nanoparticles were produced using thermogravimetric method. The most important advantages of producing NPs with this method are the reduction in the number of synthesis steps, production time and the number and costs of precursors needed, simple and inexpensive equipment, selectivity over the shape and size of the particles produced from the raw materials (metal oxides), easy control and the determination of the weight composition and process parameters in the production of Cu_x-$Ni_{(1-x)}$ and Cu_x-$Co_{(1-x)}$, (x = 0, 0.4, 0.6, 1). The reduction reaction of binary $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ mixtures, (x = 0, 0.4, 0.6, 1), with 23 Vol.% of methane at 830°C under atmospheric pressure was experimentally investigated.

The conversion time of Co_3O_4 to CoO, before the reaction with methane gas and in the presence of argon gas, is varied depending on the amount of Co_3O_4 in the samples; for samples containing higher percentages of Co_3O_4, the Co_3O_4 conversion time to CoO is greater compared to the samples containing lower amounts of Co_3O_4. The results demonstrated that the speed of the reduction reaction was relatively higher for the pellets made of nickel oxide in comparison to cobalt and copper oxides. In addition, the reduction reaction of the monometallic nano-oxide powders were relatively faster compared to binary and ternary mixtures of metal oxides. The duration of NiO, CuO and CoO reduction reaction with CH_4 at 830 °C was 14, 39 and 47 min, respectively. It was revealed that the reaction rate of the binary $(CuO)_x$-$(NiO)_{(1-x)}$ and $(CuO)_x$-$(Co_3O_4)_{(1-x)}$ mixtures with methane depends on the amount of NiO and Co_3O_4. In this regard, the reduction time of $(CuO)_{0.4}$-$(NiO)_{0.6}$, $(CuO)_{0.6}$-$(NiO)_{0.4}$, $(CuO)_{0.4}$-$(Co_3O_4)_{0.6}$ and $(CuO)_{0.6}$-$(Co_3O_4)_{0.4}$ samples were 28, 35, 39 and 42 min, respectively.

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