



Catalytic Oxidation of Carbon Monoxide Using Copper-Zinc Mixed Oxide Nanoparticles Supported on Diatomite

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ABSTRACT

Background: Diatomite coated by nanoparticles of copper and zinc mixed oxides were used to investigate catalytic oxidation of carbon monoxide.

Objectives: Aim of this paper was to investigate diatomite performance as a supporting host to confine the CuO and ZnO nanoparticles and its catalytic activity for carbon monoxide oxidation.

Materials and Methods: The prepared catalysts were characterized by Brunauer-Emmett-Teller (BET) surface area, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Catalytic behavior for CO oxidation was studied at different conditions in a tubular reactor packed with catalyst.

Results: The results illustrated that diatomite is the promising candidate for catalyst support due to its unique characteristics. The variation of catalytic activity of the prepared composite catalysts with different molar fractions of CuO and ZnO for CO oxidation in different reaction temperatures was investigated.

Conclusions: It was found that a CO conversion of 100% can be achieved at 300 °C over catalyst with 80 mol% CuO and 20 mol% ZnO content.

► Implication for health policy/practice/research/medical education:

The content and results of this paper is useful for researchers who are interested in Air Pollution Control especially catalytic elimination of carbon monoxide as a pollutant using coated Nano catalyst.

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1. Background

Carbon monoxide (CO) is produced by natural processes and anthropogenic sources. Inhalation of carbon monoxide gas can cause cardiovascular events and death (1). Catalytic oxidation of carbon monoxide is one of the most well-known methods to oxidize CO into carbon dioxide, different kinds of materials has been used for the

support of nanoparticles, some of these include: Al₂O₃, silica, MCM-48, Al-SBA-15, activated carbon fibers, Y-type zeolite and H-BEA zeolite (2-6). Diatomite is a lightweight sedimentary rock. Silicon dioxide is the main component of diatomite and some impurities such as iron, alumina and metal oxides are other components of diatomite. Diatomite has some unique characteristics such as: 80-90% pore spaces, numerous fine microscopic pores, cavi-

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ties and channels, high porosity (35-65%), good sorption ability, low density, high permeability, high surface area, excellent thermal resistance, wide variety of shape, different sizes and active hydroxyl groups on it (7-11). There are various considerable catalysts which has been supported on different oxide surfaces. Some catalysts presented in the literature are transition metal and noble metal clusters supported on Al_2O_3 , SiO_2 , TiO_2 , Fe_2O_3 (12). Heretofore the catalytic performance of diatomite supported by copper and zinc mixed oxides nanoparticles for catalytic oxidation of carbon monoxide has been never reported. Since the exploration of new catalyst systems with more inexpensive and easier available supports is still a challenge, so the aim of this paper is the investigation of diatomite performance as a supporting host to confine the CuO and ZnO nanoparticles and its catalytic activity for carbon monoxide oxidation.

2. Materials and Methods

2.1. Catalyst Preparation

The diatomite was washed with tap water to remove impurities then dried in an oven at 105 °C for 24 h. The dried diatomite was sieved to a uniform size of 0.8-1 mm. Particle size and specific surface area of CuO and ZnO nanoparticles were 60, 20 nm and 80, 90 m^2/g respectively. The following procedure was developed to insert copper and zinc oxide nanoparticles into pores of diatomite as homogeneously as possible: first the required amount of copper and zinc oxide nanoparticles placed into 200 ml deionized water to prepare different molar fractions. The mixed oxides of Cu-Zn followed this formula $[(\text{CuO})_{1-x}(\text{ZnO})_x]$, in which x equals 0.1, 0.2, 0.3, 0.4, and 0.5 which represented as $\text{Cu}_{90}\text{Zn}_{10}$, $\text{Cu}_{80}\text{Zn}_{20}$, $\text{Cu}_{70}\text{Zn}_{30}$, $\text{Cu}_{60}\text{Zn}_{40}$, $\text{Cu}_{50}\text{Zn}_{50}$, respectively, then stirring the suspension liquid for 30 min at pH of 7 at room temperature, and after that 100g diatomite was added to above solution, then gently stirring was carried out for 2h. After washing and drying at 105 °C for 24 h dried samples were calcined at different temperatures.

2.2. Catalyst Evaluation

Catalytic tests for the oxidation of carbon monoxide were carried out in a fixed-bed stainless steel tubular continuous flow reactor (3 cm inner diameter and 25 cm length) from room temperature to 500 °C and the catalyst activity was measured at steady state. The temperature being measured by a thermocouple placed into the catalyst bed. Analysis of the reaction products was carried out using a multi-component NDIR gas analyzer (Delta 1600 S-IV). The desired concentration of carbon

monoxide was obtained by regulating the air and carbon monoxide streams via trial-and-error. The conversion of carbon monoxide was given by equation 1.

$$X (\%) = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

Where C_i : inlet carbon monoxide concentration (ppm) and C_o : outlet carbon monoxide concentration (ppm).

2.3. Catalyst Characterization

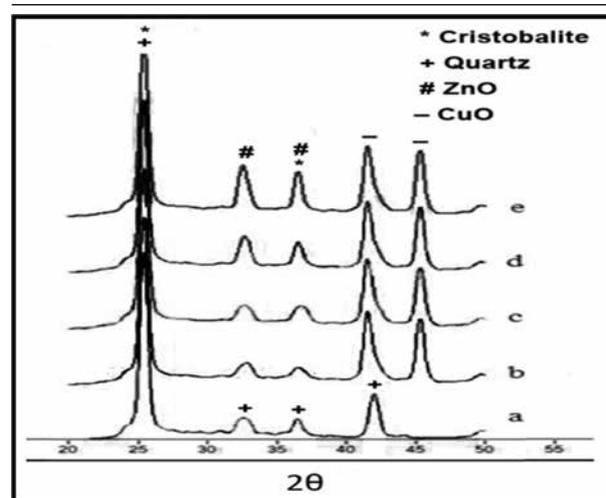
In order to determine crystal structure of the prepared catalysts X-ray diffraction (XRD) analysis was performed using Philips equipment with Cu $K\alpha$ radiation in a scanning range of 5-80° (2 θ). Elemental analysis of pure diatomite was determined by XRF technique. The surface areas of the catalysts were measured by N_2 adsorption with the BET method. Surface morphology of diatomite and coated copper and zinc oxide nanoparticles were characterized by means of scanning electron microscopy (SEM-Philips) equipped by EDX (Energy dispersive x-ray microanalysis).

3. Results

3.1. XRD and XRF Analysis

Figure 1 indicates the XRD patterns of the pure diatomite and prepared catalyst with different molar fractions of CuO and ZnO after calcinations at 450 °C. Elemental analysis of pure diatomite which was obtained by means of XRF technique is presented in Table 1.

Figure 1. XRD Patterns of the Pure Diatomite and Prepared Catalyst With Different Molar Fractions of CuO and ZnO, Calcined at 450 °C



(a) Pure diatomite; (b) $\text{Cu}_{90}\text{Zn}_{10}$; (c) $\text{Cu}_{80}\text{Zn}_{20}$; (d) $\text{Cu}_{70}\text{Zn}_{30}$ and (e) $\text{Cu}_{60}\text{Zn}_{40}$

Table 1. The Elemental Analysis of Pure Diatomite by Means of XRF^a

Component	SiO_2	Fe_2O_3	MgO	K_2O	Al_2O_3	CaO	Na_2O	TiO_2	P_2O_5
Content, %	89	1.45	0.25	0.25	2.7	0.85	3.1	0.9	1.5

^a Abbreviations: XRF, X-ray Fluorescence

3. 2. SEM Study and EDX Analysis

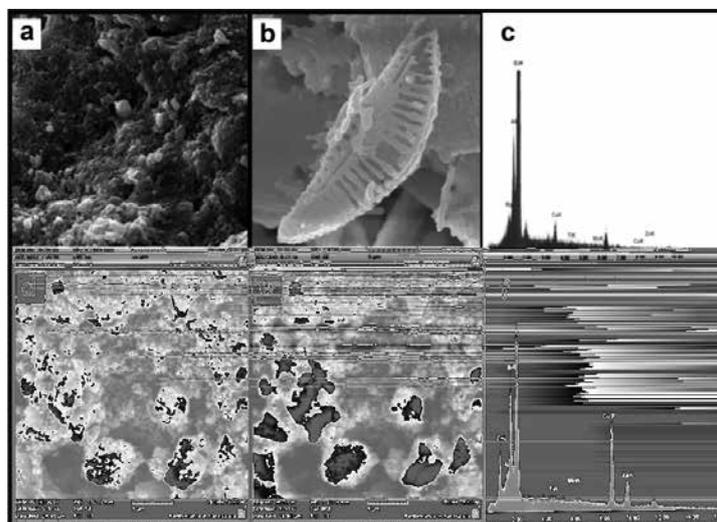
Figures 2a and b are SEM photographs of pure diatomite and Figures 2d and e are secondary electron and back-scattered of $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite respectively. Figures 2c and f are EDX analysis of pure diatomite and $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite respectively.

3. 3. Catalytic Activity

The variation of catalytic activity of the prepared composite catalysts with different molar fractions of CuO and ZnO for CO oxidation as a function of reaction temperature was investigated and the results are illustrated in Figure 3. Surface areas of catalyst samples are indicated in Table 2.

For investigating the effect of contact time on the catalytic

Figure 2. SEM and EDX Analysis of Pure Diatomite and $\text{Cu}_{80}\text{Zn}_{20}$ /Diatomite



(a) and (b) SEM photographs of pure diatomite (c) EDX of figure a (d) secondary electron of $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite (e) back-scattered of $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite (f) EDX of figure d

Table 2. Surface Area of Catalyst Samples

	Calcination Temperature, °C	Total Specific Surface Area, m^2/g
$\text{Cu}_{80}\text{Zn}_{20}$ /diatomite	300	150
$\text{Cu}_{80}\text{Zn}_{20}$ /diatomite	400	150
$\text{Cu}_{80}\text{Zn}_{20}$ /diatomite	500	148
$\text{Cu}_{80}\text{Zn}_{20}$ /diatomite	600	145
Pure diatomite	-	95

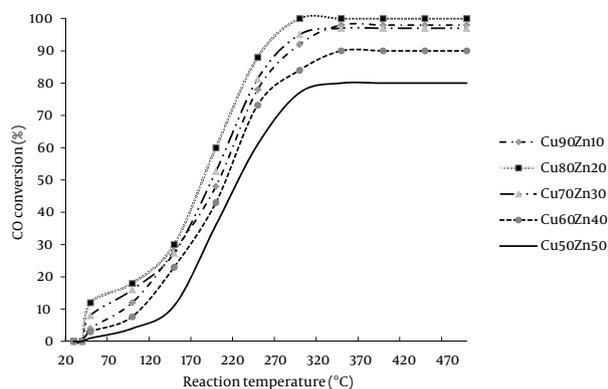


Figure 3. Catalytic Activity of Prepared Catalyst With Different Molar Fractions of CuO and ZnO, Calcined at 450 °C for CO Oxidation as a Function of Reaction Temperature

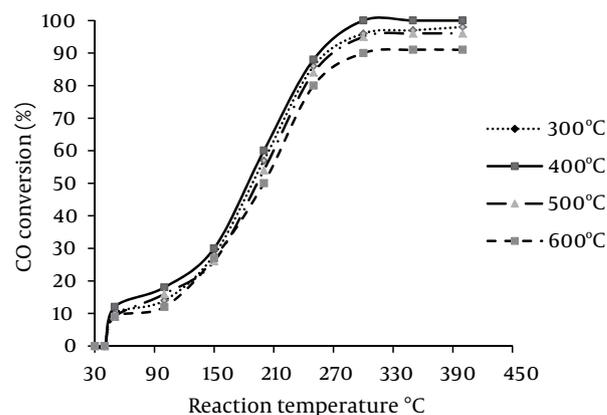


Figure 4. Influence of Flow Rate on the Catalytic Activity of $\text{Cu}_{80}\text{Zn}_{20}$ /Diatomite

activity of $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite, catalytic oxidation of carbon monoxide over this catalyst was studied at different flow rates. As shown in Figure 4, T_{50} (190 °C) is lower at low flow rate (0.5 l/min) than at a higher flow rate (1 l/min), which is due to the contact time. The reaction order of carbon monoxide oxidation was determined at T_{50} at which, the conversion of CO to CO_2 is 50% ($T_{50} = 190$ °C). The inlet carbon monoxide concentration was varied from 1 to 5%. The corresponding carbon dioxide concentration in the outlet was calculated and the data are shown in Figure 5.

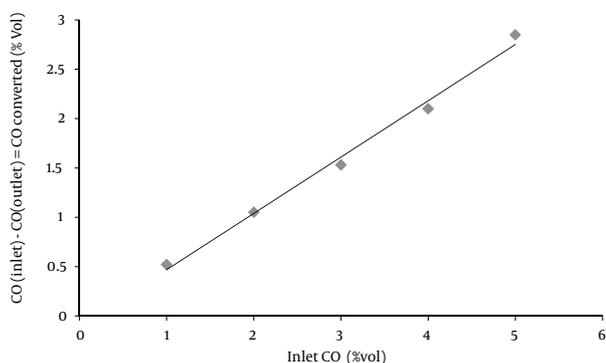
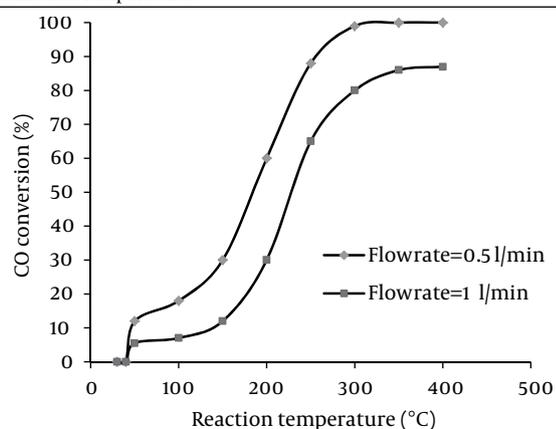


Figure 5. Determination of Reaction Order for CO Oxidation With Respect to Inlet Carbon Monoxide

Figure 6. Illustrates CO Conversion Over Prepared Catalysts at Different Calcination Temperatures



Catalytic activity of $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite, calcined at different temperatures for CO oxidation

4. Discussion

XRD and XRF analysis shows that cristobalite is the main crystal phase of diatomite as illustrated in Figure 1. Because of higher thermal and chemical stability of cristobalite (13), this crystal phase of silica is preferred to amorphous SiO_2 for applying as a catalyst support. It can be seen that CuO and ZnO peaks appear properly and the peak intensity was enhanced by increasing the nanoparticles content. As illustrated in Table 1 SiO_2 is the main component (89%) and the metal oxides (Na_2O , Al_2O_3 and Fe_2O_3) are the main minor elements. SEM study and EDX analysis declare that porous structure can be observed on the surface of pure diatomite, while after coating procedure; the surface of diatomite was covered by nanoparticles. SEM back scattered electron (BSE) image is used for illustrating contrasts in composition and to reveal the mixed oxides particles clearly. BSE image indicated a distribution of mixed copper and zinc oxides particles on the surface of diatomite. Two different zones were indicated in back scattered electron image: white zone (CuO),

and gray zone (ZnO). Si, Cu, Zn were indicated in EDX elemental analysis. Catalytic activity, as demonstrated in Figure 3, in which all catalysts indicate similar behavior as CO conversion increased with increasing the reaction temperature, while carbon monoxide conversion over pure diatomite was negligible. The catalytic activity of catalysts enhanced with increasing of ZnO content from 10 to 20 mol%, but descended with further increase of it. The $\text{Cu}_{80}\text{Zn}_{20}$ catalyst, exhibited the highest activity for CO conversion to CO_2 . It was found in previous studies that CO conversion over CuO micro powder under oxygen rich conditions and surrounding temperature of 205 °C is about 15%, (14). But the results of present study illustrated that at temperature about 200 °C, the conversion of CO to CO_2 is 60% approximately, therefore the catalyst size is a critical factor in performance of catalyst and there is a synergistic effect between copper and zinc oxides for CO conversion. The excess ZnO species have negative effect on the catalytic activity, this counterproductive effect is because of ZnO agglomeration. As illustrated in Figure 6, and performance of catalyst is nearly constant. It was found in previous studies that CO conversion over nano-sized iron oxide and $\text{CuO-Fe}_2\text{O}_3$ composite at temperature higher than 500 °C was decreased because of sintering, agglomeration of catalyst and the increase of particle sizes which decreases the number of active sites available for catalytic process (15, 16). But the present study demonstrates ability of diatomite to isolate copper-zinc mixed oxides atoms in its pores and so prevents sintering of atoms, which would greatly reduce the effective surface area of the catalyst. As demonstrated in Figure 6, the linear relationship between the effluent carbon dioxide concentration and the inlet carbon monoxide concentration indicated that the catalytic oxidation of carbon monoxide on $\text{Cu}_{80}\text{Zn}_{20}$ /diatomite is first-order with respect to inlet carbon monoxide. similar order reaction of carbon monoxide over nano-sized iron oxide have been suggested (16).

5. Discussions

A new catalyst has been prepared by simple impregnation method: filling the pores of support with a solution of copper zinc composite oxide from which the solvent is subsequently evaporated followed by drying and calcinations. The variation of catalytic activity of the prepared composite catalysts with different molar fractions of CuO and ZnO supported on diatomite for CO oxidation as a function of reaction temperature catalyst exhibited CO conversion of 100% at 300 °C over catalyst with 80 mol% CuO and 20 mol% ZnO content.

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Authors' Contribution

Saeed Dehestani Athar: 50%
Hasan Asilian: 50%

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