Review Article

Factors affecting CO oxidation reaction over nanosized materials: A review

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A B S T R A C T

The high level of carbon monoxide (CO) in the atmosphere represents a serious health and environmental problem, thus many techniques were used to reduce CO concentration. The catalytic oxidation of CO proves to be one of the most effective techniques for removing this pollutant. In this paper, we review the factors that affect CO oxidation reaction, such as catalyst crystal size, pre-treatment and preparation technique, temperature including calcination and catalytic reaction temperature, catalyst mass, and water vapor on feedstock gas. The main findings of the present review are: (1) The catalyst used in the oxidation of CO to CO₂ must have extraordinary CO oxidation activity, high selectivity, and respectable resistance toward deactivation by H₂O and CO₂; (2) Metal oxides nanoparticles are found to be favorable and effective catalysts for CO oxidation; (3) CO oxidation greatly affected by catalyst crystal size where it generally increases with reducing crystal size to a certain limit and after that the CO conversion % decrease; (4) Preparation methods affect the catalytic process as its effects on the surface area and the dispersion of the nanostructure prepared catalyst; (5) Temperature greatly affects CO oxidation catalysts. Thus, carbon monoxide catalytic materials have to work even at higher temperatures; (6) Increasing catalyst weight generally increases catalytic activity due to the increase in the total surface area and a number of active places on the surface of the catalyst; (7) H₂O vapor on feedstock gas sometimes have positive effects and other time have negative effects on the catalytic oxidation of CO. Knowing the factors that affect CO oxidation over nanosized materials will help in optimizing the condition for CO oxidation over specific nanosized catalyst.

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1. Introduction

Automotive exhaust gases formed in the gasoline engines contain many environmentally harmful compounds and with the industrialization of the third world, the number of automobiles in the world increased even more dramatically.

Unburned hydrocarbons, carbon monoxide, nitrogen oxides, and sulfur oxides are the main pollutants released from internal combustion. These gases are mainly formed due to incomplete combustion in regions of oxygen deficiency in the engine. There are also hydrocarbons emissions due to unburned fuel. Unburned hydrocarbons, carbon monoxide, nitrogen oxides, and sulfur oxides are the source of many environmental and health problems [1Y.5].

Automotive emissions can be reduced by technological improvements and modifications to the motor engines [6], fuel modifications and fuel additives [7,8], and using catalytic converters [9,10].

Motorized catalytic converters were introduced for the first time in the United States in 1974 [11] but were only shown on European roads in 1985. In fact, until 1993, the EU had not established new vehicle emission standards that effectively imposed the installation of emission control catalysts for fuel vehicles.

The basic reactions of CO and HC in the exhaust gas, at the catalytic converter surface, are oxidation to CO$_2$, while the nitrogen oxides are reduced with the desired product being N$_2$. The three main pollutants (CO, HC, and NOx) are simultaneously removed from the exhaust by a single converter at a temperature region considerably lower than flame or explosion temperatures [12]. Therefore, the catalyst used in the converter is called a three-way catalyst. Current three-way catalysts using noble metals remove 99% of CO emissions [13].

Selection of the appropriate catalyst is an essential step to improve combustion, in terms of activity and selectivity, by limiting the formation of hazardous by-products. The use of noble metals has a significant effect on the commercial cost of the entire catalyst, so the recent interest in oxide catalysts has increased considerably [14].

Despite the dangerous effect of the three main pollutants of motor vehicle exhaust for the environment, CO has proved to be the most dangerous because of its negative impact on the environment and its high toxicity to human and animal life. On the other hand, CO poisoning of platinum-based catalysts for proton exchange membrane fuel cells (PEMFC), thus requiring a reduction of carbon monoxide from the hydrogen feed stream to levels below 50 ppm before entering PEMFC. Consequently, the oxidation of carbon monoxide is a major reaction with a wide range of applications such as the elimination of the CO effect in closed air, the control of vehicle emissions and the cleaning of H$_2$ by water gas-shift and CO preferential oxidation processes [15Y.20].

Carbon monoxide (CO) is well known to have no color, no smell and to be a toxic gas at high concentration. It is a by-product result from partial combustion of fuel. CO is the chief product of the imperfect combustion of carbon and compounds containing carbon, and is one of the chief pollutants out from internal combustion engines and is the source of various environmental and health problems [21,22]. Motor automobiles release more than 66% of the synthetic CO gas in the air.

Carbon monoxide decreases the quantity of oxygen gas that reaches the blood and it may cause sleepiness, slow reflexes, impaired vision and judgment and even it may cause personal death as carbon monoxide gas replace oxygen by binding to the iron atom presented in blood hemoglobin (Hb) and so Hb becomes unqualified to carry out oxygen to the brain. More and more exposure to carbon monoxide can diminish the amount of oxygen absorbed by the brain so much that the victim may become unconscious and may suffer from brain damage or person death from hypoxia [23].

Toxicity by carbon monoxide is accompanied by some symptoms including nausea, dizziness, loss of consciousness, headache, and may reach to death [23].

Emissions from separable means of transport are generally low compared to the image of the chimney, which many people associate with air pollution, as shown in Table 1. However, in many cities across the country, the private car is one of the biggest sources of air pollution because the emissions of millions of cars on the road add up. Vehicle emissions account for about 90% of carbon monoxide emissions in large cities and about 50% of ground-level ozone. Driving with a private car is without a doubt the biggest environmental impact of a typical citizen [24].

Motorcars are one of the chief sources for urban air pollution. Consequently, the U.S. has put two concentration standard for the release of pollutants from motor vehicles. The first emission standard was proven by the environmental protection agency (EPA) and the other one, stricter, by the California air resources board (CARB). Table 2 [25Y.27] shows information on the federal CO emission standards and California CO emission standards for passenger cars.

| Table 1 – Typical concentrations of the car exhaust gas parts of gasoline-fueled engines. Air-to-fuel ratio contributes considerably to these concentrations [24]. |
|-----------------|-----------------|-----------------|-----------------|
|                |                 |                 |                 |
| HC              | 750 ppm         | CO$_2$          | 13.5 vol.%      |
| NO$_x$          | 1050 ppm        | O$_2$           | 0.51 vol.%      |
| CO              | 0.68 vol.%      | H$_2$O          | 12.5 vol.%      |
| H$_2$           | 0.23 vol.%      | N$_2$           | 72.5 vol.%      |
| * Based on C$_1$. |

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Table 2 – The U.S. emission standards for passenger cars [25Y.27].

<table>
<thead>
<tr>
<th>Emission standard</th>
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Due to the above mentioned regulations for CO emission concentration, its impacts for both human and environment, its significance in numerous fields of manufacturing significance to understand essential methods accompanying with the production of methanol, the reforming of alcohols, the water gas shift reaction, etc. [28]; examination of novel source of energy associated with the removal of carbon monoxide in hydrogen fuel cells [29]; Pollution of the environment such as, Purification of apartment and industrial air; Respirators fire fighter’s gas masks, extraction applications and protection against chemical wars; motorized emission control according to the European emission limits for gasoline engines which are existing in Table 2; clean-up of outlet gases; etc. CO oxidation has appealed renewed consideration [30Y.33].

There are many ways to remove CO, including adsorption. CO methanation and catalytic oxidation. The catalytic oxidation of CO proves to be one of the most effective techniques for removing this pollutant and many studies have been reported [30Y.35].

The objective of the present study to review the factors that affect CO oxidation reaction over nanosized materials with special attention given to the effect of catalyst chemical composition, crystal size, pre-treatment and preparation technique, temperature including firing and catalytic reaction temperature, catalyst mass, and water vapor on feedstock gas.

2. Factors affecting CO oxidation reaction

2.1. Effect of catalyst chemical structure

Environmental catalysis is a growing area of interest [36] by using a more energy-efficient alternative chemical pathway, the catalyst increases the rate at which the system moves toward thermodynamic equilibrium. Much research is devoted to the development of catalytic materials with high activity and high selectivity.

The catalysts used in the oxidation of CO to CO$_2$ are typically allocated to three classes: The first catalysts class used for conversion of CO to CO$_2$ is the noble metals such as platinum, palladium, and rhodium. which are famous CO oxidation catalysts with high catalytic activity in the temperature range from 150 to 250 A⁰C and high resistance to sintering [37Y.38].

High sulfur resistance up to 1000 ppm and interaction with the support (Al$_2$O$_3$, La$_2$O$_3$, ZrO$_2$, etc.) make the noble metal catalysts very attractive for removing the exhaust gases of motor vehicles [39Y.40]. Noble metals such as Pd, Pt and Rh have been extensively studied with supports such as cerium oxide, zirconium oxide, alumina, titania and others for the oxidation of CO [41Y.42]. Catalysts with Pt deposited on the surface of CeO$_2$ (Pt/CeO$_2$/13-Al$_2$O$_3$, Pt/CeO$_2$) have been found to have a high activity in the oxidation of carbon monoxide [43Y.44].
Pd/I3-FeMnO3 demonstrates good catalysis activity for the oxidation of carbon monoxide [45]. The activity of Pd/Al2O3 can be increased in the oxidation of CO by depositing Pd on Mn2O3 [46] or CeO2-ZrO2 [47].

The price of these noble metals and its restricted availability does not make it economically reasonable to be used and may prevent their extensive applications. Thus, preparation of more economical, affordable, and cheaper catalysts are of great importance [32].

It is now possible to reduce the specific consumption of noble metals in all their applications by modifying the catalyst to reduce the percentage of precious metals by combining noble metals with less expensive basic metals [48,49] such as Cu, Mn, Ni, Fe, etc.

The second catalysts class used in the oxidation of CO to CO2, gold catalysts and are for oxidation of CO to CO2 at very low oxidation temperature [33]. These catalysts can be functional in normal conditions, especially in air purification systems and in breathing apparatus and automotive catalysts.

The third class of catalysts used in the oxidation of CO to CO2, includes several kinds of metal oxide which were widely used for the conversion of CO to CO2 like the metal oxide of Fe, Ni, Mn, Cu, Co, Cr, Ni, Fe, etc. which can be used as separate metal oxides or in metallic combination [20,28,50Y,53].

There is a wide range of known metal oxide catalysts that initiate CO oxidation reaction such as base metals, semiconductors, spinel structure materials, hopcalite, perovskite structures, etc.

Hopcalite (50% MnO2, 30% CuO, 15% Co2O3 and 5% Ag2O) was invented by Lamb et al. [54]. These catalysts can effectively stimulate CO oxidation even at room temperature. Subsequent workers have shown that hopcalites are active at low temperatures of Y20AOC and have high durability for CO oxidation in dry conditions, but can be readily poisoned by water vapor [55Y,57].

This catalyst is very useful in respirators masks (for example, for firefighters, industry workers, scuba divers, etc.), but it does not work in catalytic converters operating at higher temperatures due to sintering.

Perovskites have a general ABO3 formula [57,58]. Where, A elements are rare earth alkaline (La, Ce, Pr) and the alkaline earth metals (Sr, Cs, Ca, Ba), while the B are full by transition metals (Co, Cu, Fe, Ni, Cr, Mn) [59]. The main advantage of perovskites lies in the fact that it has superior and activity and stability to that of simple oxides [60]. However, there are many problems with perovskites catalysts, such as thermal stability, catalytic activity, and resistance to potential toxins in fuel additives or oils such as Cl, P, and S.

Perovskite impregnation on carrier materials such as cordierite or alumina increases the surface area and consequently its the catalytic activity [40,60].

Nanomized metal and oxides are distinguished by exclusive and vital applications particularly in the catalysis field. A numeral of studies has been focused on synthesis and application of nanomaterials, metal, metal oxide, or their dual nanocomposites for multipurpose applications especially in the field of environmental pollution control and get rid of hazardous materials [61Y,71]. Recently metal oxides nanoparticles are found to be favorable and effective catalysts for CO oxidation [5,19,35,72Y,80]. The processes of catalytic conversion of CO to CO2 contain a lot of physical and chemical changes which occur concurrently and have a deep effect on each other.

The catalyst used in the conversion of CO to CO2 must have extraordinary CO oxidation activity, high choosiness, and respectable resistance toward deactivation by H2O and CO2 [81,82]. Plentiful availability of Ce and Cu, combined with their lower cost compared to noble metals, and its extreme resistance to CO2, water vapor and sulfur compounds making them powerfully competitive as a catalyst in the oxidation of CO to CO2 [83]. Recently, CuO-Y2O3 catalyst has been added to the three-way catalysts to decrease its price by lowering the amount of noble metals used in three-way catalyst [84], for the cleaning of motorized exhaust gas. Consequently, it has been thus extensively considered to substitute the expensive noble metal catalysts [85Y,87].

Copper oxide [30,88] and supported copper oxides [87,89Y,92] are extremely effective for the oxidation of CO. A great deal of research is conducted on CuO catalysts supported on: Al2O3 [89], SiO2 [90], ZrO2 [93,94], CeO2 [87,89,Y,92], TiO2 [95], etc. CeO2 as a support, acting a vital role in CuO-Y2O3 to catalyzes the complete oxidation of CO and have a catalytic activity many times greater than traditional Cu catalysts and even analogous to noble metals [93,96,97].

2.2. **Effect of catalyst crystallite size on CO oxidation**

CO oxidation greatly affected by catalyst crystal size and generally the CO oxidation extent increase with reducing the catalyst crystal size till a certain catalyst crystal size limit and after that CO oxidation % decrease with more decrease in catalyst crystal size. Catalyst crystal size alter the contact boundary between the catalyst and the support which is considered as one of the most critical factors on CO oxidation.

The alteration in the catalytic activity has been attributed to various molecular scale factors including change of surface structure, electronic state, metal-support interaction, an active surface oxide layer, oxidation states and also due to quantum confinement effects on the nanoparticle electrons, band gap change also related to quantum effects at the nanoscale size. The increase in unsaturated surface atoms due to the nanoparticle geometry also affect the catalytic activity [98]. Despite the enhancement of the catalytic activity with crystal size decreasing, this size-dependency is also representing a large limitation in the use of nanoparticles metal catalysts. At the nanoscale, melting point depression occurs to the particles, increasing the mobility of metal atoms over the support surface and increasing the probability of sintering and Ostwald ripening [99].

Previously Au was seen as an inert metal for catalysis until Haruta et al. start to study the remarkable effect of the particle size on the catalytic oxidation of CO over supported noble metals, especially gold nanoparticles [100,101]. By decreasing the crystal size of Au to less than 10 nm, Haruta et al. found that Au able to oxidize CO well below 0 AOC [102]. However, these catalysts suffer several unsolved problems, for example, deactivation in storage and indoor light, sensitivity to halogen-including compounds and its high cost [103,104]. After that strong relationship has been established between catalyst crystal size and catalytic activity in the literature [105Y,108]. For example, Halim et al. [5] investigated...
the using iron oxide, Fe₂O₃, nanoparticles, synthesized using co-precipitation method in various crystal size of 75, 100 and 150 nm with commercial Fe₂O₃, with crystal size of 250 nm, in the oxidation of CO to CO₂ and they observed that the CO oxidation extent decreased as the crystal size of the catalyst increase as shown in Fig. 1. The oxidation extent increase with time increase till it reach equilibrium and the overall CO conversions % were found to be very close to each other at the early stage of the reaction. They attributed this behavior to the homogeneity of catalyst and the availability of more active sites on the catalyst surface which affect on the catalytic activity of the catalyst. At the remaining stages of the reactions, crystallite size effect on the CO conversion appears and CO conversion % increased by decreasing the crystallite size of the catalyst. The iron oxide samples with crystallite size 250 nm show the lowest CO oxidation% and they owed this to the change in catalyst activation energy by changing the crystal size of catalyst.

Wang et al. [109] studied the influence of gold particle size on gold supported ceria catalysts for oxidation of CO and they conclude that the catalytic activity of the catalyst improved by decreasing crystal of the catalyst from 7.5 to 3.9 nm, due to the increase the contact boundary between Au catalyst and CeO₂ support where the reaction occurs. Du et al. [110] also studied the influence of gold particle size on Au supported on TiO₂ catalysts for CO oxidation and they prepare different Au/TiO₂ catalysts for CO oxidation with different Au nanoparticles sizes (5.1, 3.8, and 2.9 nm) and they found that the CO oxidation extent increase with the decrease in the Au crystal size from 5.1 nm to 3.8 nm and with more and more decrease in crystal size CO oxidation percent decrease again (Fig. 2) and the catalysts, with mean size of 3.8 nm was the most active and this is due to that, Au nanoparticles with a mean size of 3.8 nm had the greatest contact boundary with TiO₂ support, giving the widest boundary interface, proposing that the contact boundary was the most critical and important factor for oxidation of CO.

On the other hand, Nyathi et al. [111] studied the effect of crystallite size of Co₃O₄ supported on Al₂O₃ on CO oxidation by preparing Co₃O₄ catalysts with average crystallite sizes between 3 and 15 nm using the reverse micelle technique and they conclude from the obtained results that the CO oxidation activity and consequently CO oxidation percent increase with decreasing the crystal size of Co₃O₄ crystallites in a temperature up to 200 AоГ. They owed these effects to the change in the surface crystalline anisotropy with changing catalyst crystal size or from single crystals exposing different geometry.

Joo et al. [105] studied the influence of crystal size on the catalytic oxidation of Carbon monoxide over ruthenium nanoparticle catalysts synthesized by a polylol method and they found that CO oxidation activity increases with increasing the particle size of catalyst, and the catalyst with crystal size 6 nm shows 8 times higher activity than the 2 nm catalysts. Under oxidizing reaction conditions, the metallic Ru surface converts to a catalytically active thin ruthenium oxide layer which transforms into an inactive oxide phase. The observed trend of CO oxidation activity can be correlated with the stability of catalytically active core–Y₃ shell particles composed of the RuO₂ species thin layer formed on the Ru metallic core.

2.3. Effect of pre-treatment and preparation technique

The catalytic activity of synthesized metal oxide catalysts has a great dependence on the pre-treatment and preparation methods as it directly affects the surface area and the dispersion of the nanostructured prepared catalyst. The preparation methods include co-precipitation [112], combustion method [113], sol-Y₃ gel route [114] and others. Avgouropoulos et al. [115] examined the effect of preparation method on CO oxidation reaction by preparing CuOY₃CeO₂ catalysts using four preparation technique including citrate-hydrothermal, co-precipitation, impregnation, and urea-nitrates combustion methods and they found that the catalyst prepared by urea-nitrates combustion method displayed the highest catalytic activity, followed by sample prepared by citrate hydrothermal method and the one prepared by impregnation method has the lowest activity. The higher catalytic activity of the samples prepared by the urea-nitrates combustion and the citrate-hydrothermal methods is owed to the existence of well dispersed, strongly interacting with the ceria surface, copper
oxide species. However, CuO catalyst supported on CeO₂ substrate produced by Kim et al. [112], prepared by means of co-precipitation methods, of surfaces area of 91 m²/g, exhibited very high catalytic activity in PROX, where it lower CO concentration to no more than 100 ppm at temperature up to 170 AοC in a mixture containing 50% H₂, 1% CO, or 1.25% O₂ and the remaining is water and carbon dioxide.

Jianjun et al. [116] studies the preparation method effect and calcination temperature on the oxidation of CO over Co₃O₄ catalyst supported on CeO₂ at low-temperature and they prepare Co₃O₄ supported CeO₂ mixed oxides with numerous of preparation methods like co-precipitation oxidation, homogeneous precipitation, and complexation combustion methods. The catalysts were used for CO oxidation under dry and humid conditions and at low temperature. TheCo₃O₄ catalyst supported on CeO₂ prepared by the co-precipitation-Y₂O₃/oxidation technique and calcined at 538 K showed tremendous activity for CO oxidation among the tested catalysts and resist water vapor poisoning as this catalyst had extraordinary distribution, small particle size, and greatest surface area.

Gong et al. [117] follow the effect of preparation methods of mixed oxides of CeO₂ and MnO₂ on preferential oxidation of CO in H₂-rich gases (CO-PROX) over CuO catalysts and in their study they synthesized CeO₂-Y₂O₃ mixed oxides by surfactant-template (CB) and deposition-Y₂O₃ precipitation (DP) methods. The prepared CeO₂-Y₂O₃ was used as a support of CuO catalysts. The results that they obtain confirm that preparation technique of CeO₂-Y₂O₃ support give an uninterrupted effect on catalytic activities of CuO supported on CeO₂-Y₂O₃ catalysts and CuO catalyst supported on CeO₂-Y₂O₃ prepared by surfactant-template shows the highest stability and CO oxidation extent in H₂-rich gases than CuO catalyst supported on CeO₂-Y₂O₃ prepared by deposition-Y₂O₃ precipitation, where it give 100% CO conversion percent at 140 AοC, which specifies that CeO₂-Y₂O₃ support prepared by surfactant-template and more valuable on preferential oxidation of CO in H₂-rich gases than CeO₂-Y₂O₃ support prepared by deposition-Y₂O₃ precipitation where CuO supported on CeO₂-Y₂O₃ (CB) were found to have more Mn⁴⁺ species and richer on oxygen vacancies, also there is strong interaction in between CeO₂ and MnO₂ on its surface. More amounts of active copper species and complicated transfer of CuO/CeO₂-Y₂O₃ (CB) electrons density also enhance the catalyst activity and this can be also attributed to that CeO₂-Y₂O₃ (CB) support prepared by surfactant-template method holds a larger BET surface area (148 m²/g) and smaller particle size (3.6 nm), compared with CeO₂-Y₂O₃ (DP) (91.2 m²/g) and crystal size (5.9 nm).

Four catalysts sample having the same composition (CuO/Co₃O₄-ZrO₂/Al₂O₃) were prepared using four variant approaches and surveyed for oxidation of CO by Ram Prasad et al. [94]. The four catalysts were synthesized by citric acid sol-Y₂O₃, impregnation, urea gelation co-precipitation, urea nitrate combustion methods. The catalytic performance of the catalyst synthesized using sol-Y₂O₃ technique displays the highest catalytic routine, and this can be attributed to the homogenous distribution of the Cu species in the CuO/Co₃O₄-ZrO₂/Al₂O₃ sample, while the catalyst synthesized by urea nitrate combustion process has the worst performance as a result of sintering and the catalyst prepared by sol-Y₂O₃ method show CO catalytic activity higher than the catalyst prepared by co-impregnation and the catalyst prepared by co-impregnation method show CO catalytic activity higher than the catalyst prepared by urea gelation the catalyst prepared by urea gelation method show CO catalytic activity higher than the catalyst prepared by urea nitrate combustion processes. The four prepared catalysts are very active for the oxidation of CO even after 50 h of nonstop run at 200 AοC.

It was also found that using ethanol as a dehydrating agent in co-precipitation technique led to prepare catalysts with the greater surface area, reduced particle size and superior catalytic activity [118]. Liu et al. [119], for example, study the impact of ethanol washing in precursor of preparing CuO-Y₂O₃ catalysts in preferential oxidation of CO in the presence of excess hydrogen (PROX) and they found that The CO oxidation extent over CuO catalyst supported on CeO₂ substance without washing by ethanol reach about 85% at 190 AοC, while the maximum CO oxidation extent over CuO catalyst supported on CeO₂ washed by 200 mL of ethanol reached approximately 99% at 120 AοC. The catalyst characterization using XRD and TPRF showed that washing CuO supported on CeO₂ with ethanol prevent the grain growth of CuO supported on CeO₂ catalysts and enhance the reducibility of CuO supported on CeO₂ catalysts and increase the spreading and surface area of the synthesized catalyst. Characterization of the catalyst using FTIR measurement demonstrated that the water absorption decrease and consequently the amount water linkage between adsorbed water and CuO supported on CeO₂ catalyst’s precursor was diminished by the way of ethanol washing, and this prevents the grain growth of CuO-CeO₂ catalysts.

The pre-treatment of the catalyst also affect the oxidation reaction. For example, Sun et al. [120] studied the influence of calcination temperature and copper precursor on CO oxidation over CuO supported on CeO₂ catalysts prepared using impregnation method using diverse Cu precursors including sulfate, acetate, chloride, and nitrate and fired at 500 or 800 AοC. The Copper acetate prepared CuO/Co₃O₄ and fired at 500 AοC displays the highest activity for oxidation of CO, as a result of stronger synergistic effects and the existence of intensely dispersed CuO. The synergistic effects can encourage the formation of Cu⁺ ions which are the best sites for CO adsorption, and motivate the oxygen of the network and thus play an essential role in CO catalytic reaction progression. However, the remaining SO₄²⁻ and Cl⁻ have an undesirable effect, which leads to low CO oxidation activity. Upon calcination of catalysts at 800 AοC, Cu⁺ ions species obtained from all Copper precursors are predominantly bulk CuO. Thus, the catalytic activities of these catalysts decrease than the catalysts fired at 500 AοC, with the exception of CuO/Co₃O₄ catalyst prepared from sulfate precursor calcined at 800 AοC is even more active than CuO/Co₃O₄ from sulfate precursor fired at 500 AοC owing to the development of CuO from the breakdown of inactive CuSO₄ and elimination of SO₄²⁻ site-blocking radical. CuO/Co₃O₄ prepared from chloride precursor calcined at 800 AοC with lower content of CuO shows improved catalytic activity more than CuO/Co₃O₄ from acetate precursor calcined at 800 AοC and CuO/Co₃O₄ from sulfate precursor calcined at 800 AοC further representing that the CuO in the...
catalyst bulk has only a slight influence on the catalytic activity [120].

Al$_2$O$_3$/CeO$_2$ doped by Fe$_2$O$_3$ [52] was synthesized by co-precipitation technique and used as support for Gold nanoparticles which was loaded to its surface by the deposition precipitation method. Both the thermal stability and catalytic activity of gold catalyst were enriched meaningfully by doping with Al$_2$O$_3$/CeO$_2$. The catalyst doped by 1% of gold particles and fired at 180 AøC completely oxidizes CO at Y 8.9 AøC, whereas the catalyst modified with Al$_2$O$_3$/CeO$_2$ exhibited complete CO oxidation at Y 20.1 AøC. Al$_2$O$_3$/CeO$_2$ doping inhibits the mesoporous catalyst structure from collapse during the high-temperature calcination process, resulting in reducing the pore size and a higher catalyst specific surface area. The Au particles in Au/Fe$_2$O$_3$ crystal size was about 7 nm and the support crystal size ranged from 50 to 100 nm after calcination at 500 AøC. Although the particle size of the Au in Al$_2$O$_3$/CeO$_2$ doped by Fe$_2$O$_3$ was about 5.1 nm and the support crystal size extended from 10 to 30 nm, Au loaded on the Fe$_2$O$_3$ support on Al$_2$O$_3$/CeO$_2$ substrate have superior CO oxidation’s catalytic activity.

2.4. Effect of temperature

Temperature has become an increasingly important factor for the deactivation of catalysts as it may effect on the formed metal oxide, support phase, and oxidation state, the degree of crystallization, crystallize size and reduction in the surface area of catalyst per unit mass due to sintering on exposure to high temperatures. Thus, carbon monoxide catalytic materials have to work even at higher temperatures.

2.4.1. Effect of calcination temperature

Calcination temperature was found to affect on both the formed metallic phase, crystal size and consequently on the surface area of the prepared catalyst. Abdel-Halim et al. [121] found that calcination temperature to somewhat affect the CO catalytic oxidation reaction over the nanocrystalline powders of the metal ferrite of Cu and Mn. On the other hand, they observed that the catalytic oxidation of CO by means of CuY,Mn ferrite enhanced by increasing firing temperature from 1000 AøC to 1200 AøC and they owed this change to complete formation of the ferrite phase and high degree of crystallization at high temperature. In contrast, the catalytic CO oxidation activity of FeY,Co mixed oxides drops with increasing the calcination temperature from 400 to 600 AøC as shown in Fig. 3 as a result of the growth in crystallize size and decreasing surface area of the catalyst with increasing firing temperature and also formation of cobalt ferrite CoFe$_2$O$_4$ spinel with small surface area and large particle size. The FeY,Co calcined at 400 AøC (FC-400) achieve complete CO oxidation at 175 AøC while FeY,Co calcined at 600 AøC (FC-600) achieve complete CO oxidation at 200 AøC [122].

Calcination temperature was found also to affect the formed metal oxide, support phase, and oxidation state and Chang et al. [123] observed that CeO$_2$ and Au/CeO$_2$ heat treatment has a reflective effect on the oxidation of CO to CO$_2$ and the CO oxidation percent increase from 72% to 99% by increasing the CeO$_2$ firing temperature from 200 AøC to 400 AøC and they attributed this to the increase the concentration of Ce$^{4+}$ species from 82% to 85% with increasing the temperatures of calcinations from 200 AøC to 400 AøC. CeO$_2$ samples fired at 400 AøC shows high catalytic activities and this could be owed to the increase in Ce$^{4+}$ concentration and the crystalline CeO$_2$ structure when fired at a higher calcination temperature. Also, Hutchings et al. [124,125] studied the catalytic CO oxidation over Au/Fe$_2$O$_3$ catalysts and they found that the uncatalyzed catalyst was the most active, relative to the calcined one due to the presence of both cationic Au$^{3+}$ and metallic gold, while the support was mainly ferrihydrite, Fe$_2$HO$_2$Al$_6$H$_2$O. The mechanism of the CO oxidation was proposed to proceed via carbonate intermediate. The calcined catalyst of lower activity showed the presence of Au supported on α-Fe$_2$O$_3$. The influence of calcination temperature on Au supported on CeO$_2$ support was also testified by Park et al. [126], which specified that the Au nanoparticles oxidation states were influenced by both the firing temperature and by the interactions between Au catalyst and CeO$_2$ substrate and that the heat treatment influence on the oxidation of CO after loading the gold catalyst on CeO$_2$ support is more significant than the influence of calcination temperature on CeO$_2$ alone.

2.4.2. Effect of catalytic reaction temperature

Catalytic CO reaction temperature was found to affect on CO conversion % as it may lead to catalyst sintering or Hydrogen depletion in case of CO oxidation in the hydrogen-rich atmosphere. Halim et al. [5] found that the catalytic CO oxidation temperature shows an important role in the CO oxidation to CO$_2$ over nanosized Fe$_2$O$_3$. On relatively high reaction temperatures of 400Y,500 AøC, it was detected that all samples Y, (tm) response toward the oxidation of CO increases with increasing catalytic temperature till 400 AøC and it decreases again at a higher temperature of 500 AøC due to sintering effect. Soliman et al. [53] also studied the influence of temperature on the oxidation of CO over nano-sized CuOY,Fe$_2$O$_3$, CuOY,CeO$_2$, CuOY,Fe$_2$O$_3$Y,CeO$_2$Y,Al$_2$O$_3$ and CuOY,CeO$_2$Y,Al$_2$O$_3$ and they found that the catalytic oxidation temperature is considered to be the main factor affecting the overall rate of oxidation of CO to CO$_2$ as shown in
Table 3 – Effect of temperature on CO conversion % over 0.3 g of catalyst (16% CO initial flow rate) [53].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>300 AoC (CO Conv.%)</th>
<th>400 AoC (CO Conv.%)</th>
<th>450 AoC (CO Conv.%)</th>
<th>500 AoC (CO Conv.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuOY₆Fe₂O₃</td>
<td>26</td>
<td>48</td>
<td>28.8</td>
<td>52.8</td>
</tr>
<tr>
<td>CuOY₆CeO₂Y₆Al₂O₃</td>
<td>72</td>
<td>100</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>CuOY₆CeO₂</td>
<td>60</td>
<td>100</td>
<td>85</td>
<td>87</td>
</tr>
<tr>
<td>CuOY₆CeO₂Y₆Fe₂O₃Y₆Al₂O₃</td>
<td>48</td>
<td>96</td>
<td>98</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Table 4 – Effect of catalyst mass on the CO oxidation at 300 AoC and 5% CO initial flow rate [53,128].

<table>
<thead>
<tr>
<th>Catalyst weight</th>
<th>0.3 g</th>
<th>1 g</th>
<th>2 g</th>
<th>3 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO conversion % over CuOY₆CeO₂Y₆Al₂O₃</td>
<td>74%</td>
<td>80%</td>
<td>82%</td>
<td>98%</td>
</tr>
<tr>
<td>CO conversion % over CuOY₆CeO₂Y₆Fe₂O₃Y₆Al₂O₃</td>
<td>48%</td>
<td>62%</td>
<td>75%</td>
<td>80%</td>
</tr>
</tbody>
</table>

Fig. 4 – The relation between oxidation temperature and CO oxidation extent over (Copyright (2014) international journal of advanced research) [53]; (A) CuOY₆Fe₂O₃; (B) CuOY₆CeO₂Y₆Al₂O₃; (C) CuOY₆CeO₂; (D) CuOY₆CeO₂Y₆Fe₂O₃Y₆Al₂O₃.

Fig. 5 – Effect of catalyst mass on the CO oxidation at 300 AoC at 300 AoC and 5% CO initial flow rate over CuOY₆CeO₂Y₆Fe₂O₃Y₆Al₂O₃ [128].

2.5. Effect of catalyst weight

Generally, increasing catalyst weight increase the conversion % as a result of increasing the total surface area of the catalyst. Soliman et al. [53,128] for example, studied the effect of catalyst weight for CuOY₆CeO₂Y₆Al₂O₃ and CuOY₆CeO₂Y₆Fe₂O₃Y₆Al₂O₃ catalysts on CO oxidation, and they found that the CO oxidation extent increases by increasing catalyst mass from 0.3 to 3 g as shown in Table 4 and Fig. 5. The CO conversion % increase from 48% to 80% with increasing the catalyst weight from 0.3 to 3 gram, they attributed this behavior to the increase on the total surface area and number of sites available for reaction on the catalyst surface which intern enhances the adsorption of CO and O₂ on the catalyst surface followed by dissociation of O=O bonds, and after that CO attract the dissociated O atom to form CO₂ molecules.

Abdel Halim et al. [5] also studied the effect of catalyst mass on CO oxidation extent and they found that there is best weight for the catalyst on CO oxidation extent above which further increase in weight not considerably affects the conversion percent as shown in Fig. 6 where CO conversion percent for different weights of Fe₂O₃ at temperature 200 and 400 AoC,
respectively, and they detected that almost all catalyst weights display the same trend on the oxidation of CO up to 35% in the early stages of the reaction, then an asymmetric shift is observed until the end of the reaction experiment and that 3 g of Fe₂O₃ samples show the extreme rate at the final stages and 2 g of Fe₂O₃ catalyst shows the highest oxidation extent.

2.6. Effect of water vapor

Generally the gas used in CO oxidation experiment often contains unavoidably amount of H₂O vapor and numerous researches have been conducted to examine the impact of H₂O vapor on the oxidation of CO, but even though of these efforts till now there are many hidden parts on understanding the effect of H₂O vapor in the oxidation of CO. H₂O vapor on feedstock gas sometimes has positive effects and other time have negative effects [85, 129Y, 139, 115, 140]. Generally, the amount of moisture adsorbed on the catalyst mainly determines the activity. Low H₂O vapor content was favorable to the oxidation of CO, while greater H₂O vapor content case a reduction in the catalyst activity. Water vapor may have a negative effect on using porous support materials where water vapor molecules block the active sites and form the less active COY-H₂O surface complexes at the catalyst surface. The positive effect of water vapor on CO oxidation can be classified into four classes: the first class, creation of active sites, the second class, direct involvement in CO₂ formation by direct involvement of H₂O and OH⁺ groups in CO oxidation, the third class, activation of O₂ molecules via OOH formation, and last one, transform carbonates, catalytic intermediates and inhibitors, into bicarbonates to accelerate decomposition [141, 142]. Which class of the above predominate during CO oxidation reaction depend on firing temperature and type of support. For example, Au supported on TiO₂, MnO₂, Fe₂O₃, Co₃O₄ or NiO, the third class is the most prevailing, while on Au supported on Mg(OH)₂ or La(OH)₃ the second class predominate. Water vapor sometimes does not directly affect catalytic CO oxidation but the carbonate species are accumulated at Au nanoparticles and metal oxide support surface, resulting in the reduction in the reaction rate. However, the carbonate species decomposes by water vapor, leading to the enhancement of the CO oxidation reaction [126, 129Y, 135, 142].

H₂O vapor on the CO oxidation reaction sometimes has positive effects and other time have negative effects on using Au catalysts. DataA(c) et al. [143, 144] examined the influence of H₂O vapor on the catalytic CO oxidation activity over Au catalyst supported on TiO₂ and they found that at low H₂O vapor content, from 0.1 to 200 ppm, was favorable to the oxidation of CO, while greater H₂O vapor content, up to 6000 ppm, case a reduction in the catalyst activity due to the blocking of the active sites. Moisture improves the reaction by more than 10 times up to 200 ppm H₂O, while further increase in the moisture content retards the reaction as shown in Figs. 7 and 8. On the other hand, H₂O has a helpful effect in preferential oxidation of CO in the presence of excess hydrogen (PROX) gases, if TiO₂ exchanged by α-Fe₂O₃ [145].

For Pt catalysts, the types of the supports are the guiding factor in the effect of H₂O vapor in the oxidation of CO or in preferential oxidation of CO in the presence of excess
hydrogen (PROX) gases. Using metal oxides like Al₂O₃ support \[129,133,146\], encourage the positive effect of water vapor on the oxidation of CO or CO-PROX. The presence of H₂O significantly improves CO oxidation over Pt catalyst supported in the I₃-Al₂O₃ substrate in temperature range from 110 AOC to 190 AOC \[146\]. In contrast, the undesirable effect of H₂O vapor was detected on using a number of porous support materials \[138\] like C as support for Pt, Ru catalysts as the water vapor molecule cover the active sites and formation of less active CO₂H₂O surface complexes at the catalyst surface.

H₂O vapor has only retarding effect on the oxidation of CO or CO-PROX over metal catalysts other than noble metal, particularly Cu and Ce containing catalysts \[85,115,140\], which was attributed to the overcrowding of active surface sites over the catalyst surface by the adsorbed water vapor molecules.

3. Conclusions

Metal oxides nanoparticles are found to be favorable and effective catalysts for CO oxidation. CO oxidation greatly affected by catalyst crystal size and generally the CO oxidation extent increase with reducing the crystal size of the catalyst till certain limit and after that, the CO oxidation % decrease with more decrease in catalyst crystal size. The contact boundary between the catalyst and the support, the surface area and the dispersion of the nanostructured prepared catalyst are the most critical factor on CO oxidation. Carbon monoxide catalytic materials have to work even at higher temperatures and not affected by calcination and reaction temperature. Increasing catalytic reaction temperature generally increases the CO conversion % unless it leads to sintering of the catalyst. Increasing catalyst weight increases the catalytic activity due to the increase in the total surface area and the number of active sites on the catalyst surface. Amount of moisture adsorbed on the catalyst mainly determines the catalyst activity. H₂O vapor on feedstock gas sometimes has positive effects and other time have negative effects.

Conflicts of Interest

The author declares no conflicts of interest.

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