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CARBON MONOXIDE OXIDATION USING COBALT CATALYSTS: A SHORT REVIEW

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Received: October 21, 2013 / Revised: November 25, 2013 / Accepted: February 02, 2014

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Abstract. The preparation methods and main characteristics of known catalysts for carbon monoxide oxidation have been examined. A short review in a tabular form which facilitates a quick view on catalysts for CO oxidation (mainly cobalt ones) is represented.

Keywords: cobalt, catalyst, carbon monoxide, oxidation, catalytic convertor, automobile exhausts.

1. Introduction

Carbon monoxide is an odourless, colourless and toxic gas. It is about 3 % lighter than air, therefore it is impossible to see, taste or smell the toxic fumes. It is also called as a silent killer. It is a non-irritant gas and is slightly soluble in water. It is generally produced and released from the partial combustion process of fossil fuel. For instance, during the cold start period of vehicles, a lot of carbon monoxide (CO) is released in atmosphere [1]. It is also a common industrial hazard created due to incomplete combustion of any carbon based fuel, such as coal, petrol, diesel, liquefied petroleum gas (LPG), natural gas, charcoal and wood [2]. Umpteen numbers of other sources are there which add carbon monoxide to the atmosphere such as gas appliances (ovens, stoves, dryers), liquid propane fuelled equipment, tobacco smoke, house fires, blocked chimneys, charcoal grills, *etc.* Carbon monoxide is responsible for a large percentage of the accidental poisonings and deaths reported throughout the world each year [3]. Certain conditions exist in both the indoor and outdoor environments that cause a small percentage of the population to become exposed to dangerous levels of carbon monoxide. High levels of CO can be fatal causing death within minute, *i.e.* carbon monoxide reacts or binds with the haemoglobin (which is responsible for oxygen carrying) to form carboxyhaemoglobin which greatly reduces oxygen

carrying capacity, because CO has more affinity to react with haemoglobin than O₂. Hence if there is a lot of CO in the air, the body may replace oxygen in blood with CO. This blocks oxygen from getting into the body, which can damage tissues and result in death [4].

The efforts made in the last century for the abatement of pollution from the mobile sources are still in progress. The catalytic oxidation of CO to CO₂ is a reaction that has been studied especially by automotive industry [5-6]. Numbers of parameters are responsible for pollution created by mobile sources. The effectiveness of catalytic converters depends on the exhaust gas temperature, which is fairly low during cold-start [7-10]. Therefore the emissions of pollutants are very high during the cold start [11]. Cold start emission depends on numbers of factors [5] such as misfiring, incomplete flame propagation, wall wetting, rich fuel/air charge, crevice storage of the fuel/air charge and its release, oil dilution with liquid and fuel vapour, wall quenching, poor post-flame oxidation, exhaust valve leakage, inlet valve leakage and lubricating oil. In order to tackle the problem of cold start various studies have been done [2, 12-13]. Along with CO, VOCs are another form of pollutants that comes out during cold start [11]. Climate change is a serious environmental challenge and stringent regulations have been adopted by the Government from time to time to tackle it [4]. They have set mandatory reduction targets for all major industries that produce greenhouse gases, like carbon dioxide, that cause climate change. The challenges for the researchers are to make or develop such methods which can be used for the generation of the clean energy which is required by the growing industries. The methods that are used till date in many industries lead to air pollution which adds harmful products like NO_x, smog, smoke, VOCs, CO, HC, CO₂, *etc.* to atmosphere. Various catalysts have been developed for VOCs [14-16] and NO_x [17-18] removal. Sources used in industries for

energy generation should be substituted for the eco friendly fuels. Coal is used for generation of energy at power plants. Coal contains sulphur which results in SO_x which in turn is responsible for the acid rain, smog formation, etc. Various equipments are available for the removal of particulate matters, conversion of harmful gases into less harmful ones, but the treatment of these pollutants is so expensive that the products would not be feasible in economic terms under those conditions. So, we have to develop the techniques which are less expensive compared to the present scenario. Another source of air pollution is from the household activities in rural or urban areas. In the last three decades various norms were employed and amended from time to time in order to check the air pollution, but we are still lacking them due to improper management.

2. Catalysts for CO Oxidation

In literature many catalysts including base metals, noble metals, nano-catalyst and mixture of base and noble metals have been reported for CO oxidation.

A good catalyst should have high activity, selectivity, thermal characteristics, stability, mechanical strength and low cost [19]. For the present study the types of catalyst used for CO oxidation can be divided as follows:

1. Noble metals catalysts
2. Base metals catalysts
3. Perovskites

2.1. Base Metal Catalysts

Base metal catalysts have been considered as an alternative for CO oxidation because they also exhibit the same characteristics as those of the noble metal catalysts at elevated temperatures. They are deposited on the support which is generally a cheap compound having a very high surface area per unit gram of the catalyst. Transition metals are usually used as a precursor. They are embedded on the support which makes the reaction feasible for a particular reaction. Various transition metals such as copper, cobalt, ceria, zirconium, manganese, iron, etc. are used for the catalyst preparation. Researchers all around the world have tested and explored these base metals for CO oxidation. In 1920 W. Bray [20] for the first time reported a catalyst hopcalite [21-23] which can oxidise CO and later on it was tested for many reactions that include oxidation. Hopcalite is basically a mixture of base metals (50 % MnO_2 , 30 % CuO , 15 % Co_2O_3 and 5 % Ag_2O) and has many applications in day to day life as well. After the discovery of hopcalite just of the need for CO conversion to CO_2 in the air, it was found that the

activity of gold based catalyst was increased with the addition of small amount of base metals (copper) [24]. With time, a lot of advancements have been done by the researchers by substituting different base metals for the hopcalite which enhances its catalytic activity by varying the composition, different methods of preparation, addition of promoters and stabilizers. Effects of alumina support on cobalt catalyst were studied [25] by varying the synthesis methods revealed that the catalyst prepared by the impregnation methods has a high activity. The oxidation of CO over $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ at room temperature studied by [26] reported that the pre-oxidised catalyst shows the higher activity for CO. The comparative study of CO oxidation by using three different metals was also done by H. Matralis *et al.* [27]. Three different catalysts were $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ and CuO-CeO_2 . It was shown that at relatively low reaction temperatures $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ catalyst is superior to other two ones for the selective CO oxidation.

2.2. Noble Metal Catalysts

Automotive industry utilizes large amounts of precious metal catalysts because of their high activity and selectivity and stability under various reaction conditions. They do not form oxides under normal conditions, *i.e.* the oxides of noble metals are not stable. Noble metals were used for the first time for the oxidation of CO by Cohn *et al.* [23] and the advancement of these processes is still going on in order to undergo 100 % completion of CO at low temperature. These catalysts are used because of their ability to disperse nano-scale precious metal particles on supports with high surface area such as carbon, silica, and alumina. Noble metals such as platinum, palladium, gold and rhodium with various supports are used in a catalytic convertor (described below) for the oxidation of CO and have been studied by umpteen number of researchers in order to improve their activity and to make them economical. The supports used are alumina, magnesium, silica, etc. [24, 29, 30]. In 1965 G. Cohn [28] proposed $\text{Pt}/\text{Al}_2\text{O}_3$ as a catalyst for the oxidation of carbon monoxide which later on was studied and reported by many researchers. U. Olsbye *et al.* [31] prepared the catalyst of platinum supported on alumina by various methods. The kinetics of CO oxidation on platinum was studied [32], a reaction mechanism for the oxidation and CO reduction on the platinum surface was described [33] and ultra fine gold particles which were very active for H_2 and CO were prepared [34]. The particles were supported by different supports of base metals which were active even at the temperature as low as 203 K. H. Igarashi *et al.* [35] reported the oxidation of CO over platinum catalyst supported on zeolite. M. Ozawa *et al.* [36] studied CO oxidation over Pt/Ce-Zr oxide catalysts with a low content of platinum

and cerium components and the results showed that highly dispersed platinum particles and the oxygen storage capacity of ceria and zirconium contributed to the high catalytic activities of CO oxidation.

2.3. Perovskites

In 1970 D. Meadowcroft [37] for the first time described the use of perovskites in zinc air batteries. One of the greatest advantages of perovskites is that they have high oxygen coverage on the surface depending on binding energy for oxygen. They can release and take up oxygen in a reversible way [38]. Various mechanisms were also described for oxygen mobility on these surfaces [39]. The general formula of these oxides is ABO_3 in which the cation A (La, Ce, Pr, Cs, Sr, Ba, Ca) of a larger size is responsible for the thermal resistance of the catalyst, whereas the cation B (Co, Fe, Cu, Ni, Mn, Cr) of smaller size accounts for the catalytic performance. Various methods in literature are available for synthesis of these catalysts [40]. Among the possible compositions, cobalt and manganese based perovskites are highly active [41–42]. Therefore extensive amount of work has been done on perovskites catalysts containing cobalt which helps in CO oxidation [43].

2.4. Three-Way Catalytic Converter

Catalysts that are used for catalytic combustion are mainly noble metals, very active at low temperature, as they play the major role in the three way catalytic converter. The three noble metals that are used there are: platinum, palladium and rhodium [44]. Due to a partial combustion, gases entering inside the catalytic converter consist of a mixture of CO, unburned hydrocarbons (HC) and oxides of nitrogen (NO_x), which are harmful for environment. The catalytic converter consists of two ceramic blocks with microducts which are used in order to increase the contact zone between gasses and the catalyst. The increase in surface area is greater than the area of football field. The ducts consist of platinum and rhodium in one block while platinum and palladium in the other one, acting as catalysts. As the gas enters inside, nitrogen molecules are first to react. The catalyst causes the oxides of nitrogen to reform into nitrogen and oxygen, respectively. The gas then flows through the microducts of the 2nd ceramic block where it reacts with platinum and palladium. Inside the microducts of the 2nd ceramic block, CO and unburned hydrocarbons react with oxygen molecule to form carbon dioxide and water vapours. The unburned hydrocarbons also react with oxygen to form water and carbon. And hence, exhaust gases now becomes less toxic having the mixture of CO_2 , N_2 and water vapours. However, their use is not up to the mark in terms

of high price, low thermal stability and tendency to poisoning. There is decrease in the activity of the catalyst with time and the development of any catalyst requires an economic consideration according to the usage of the catalyst. The activity of the catalyst has been neglected many times keeping in view its poisoning, maintenance and regeneration problem. Various factors are responsible for deactivation of the catalyst such as: 1) deposited poisons that cover the active sites of the catalyst and partially plug the pore entrance; 2) chemisorbed poison which is the result of the compounds that are present in the reactant gasses such as sulphur which chemisorbed on the catalyst surface. The three-way catalytic converter has the same problem of poisoning; 3) diffusion poisons that result due to blocking the pore mouths of the catalyst and prevent the reactant from diffusing into the inner surface of the catalyst.

2.5. Preparation Methods

If we rearrange the atoms in coal, we get diamonds. If we rearrange the atoms in sand (and add a pinch of impurities) we get computer chips. If we rearrange the atoms in dirt, water and air we get grass. Similarly catalysts are made up of atoms and its activity depends upon how those atoms are arranged. By numerous studies it has been established that the preparation method could exert a basic influence on the structural properties of the catalysts, like surface area, component dispersion and strength of interaction, which in turn determines the redox properties and reactivity of the final catalysts. Therefore methods of preparation are also developing at a faster rate as that of the development of new catalysts. There are various methods for preparation of the catalyst [45]:

1. Wet impregnation method.
2. Co-impregnation method.
3. Precipitation deposition method.
4. Co-precipitation of Cu and Ce method.
5. Urea gelation method.
6. Urea nitrate combustion method.
7. Solution combustion method.
8. Citric acid sole-gel method.
9. Surfactant assisted method.
10. Solvothermal method.
11. Leaching method.
12. Chelating method.
13. Inert gas condensation (IGC) method.
14. Electroless method.
15. Laser vaporization and controlled condensation.
16. Solvated metal atom impregnation method.
17. Combinatorial synthesis of mixed metal oxides.
18. Chemical vapour deposition.
19. Reverse micelle method.
20. Modified reverse-phase microemulsion method.

21. Gas phase grafting method.
22. Liquid phase grafting method.
23. Co-sputtering and position.
24. Alternate method.

2.5.1. Chemical vapour deposition (CVD) technique

There is no inference of solvent and no need of drying by using CVD method. The advantage over the traditional impregnation method is that any hazardous waste is also eliminated if present. These methods may also offer a better control of the precursor adsorption process.

a) Atomic layer deposition. Precursor is chemisorbed on the support, this technique was previously known as the atomic layer epitaxy (ALE) [46]. The reactants to be chemisorbed must be volatile and thermally stable at reaction temperature. When the conditions of self-terminating surface reactions are fulfilled, only reactions between functional groups at the surface and the catalyst precursor occur.

b) Gas phase adsorption technique was adopted by A. Rautiainen *et al.* [47] and described that both Co/SiO₂ and Co/Al₂O₃ catalysts were prepared by chemisorption of cobalt acetylacetonates, Co(acac)₂ or Co(acac)₃ from the gas phase onto the support. The support was kept in a fixed bed and the precursors were evaporated at 443 or 453 K. Nitrogen was used as a carrier gas for chemisorptions of precursors on the support. The catalyst preparation by ALD consisted of the following subsequent steps: a) preheating of the support; b) chemisorption of the gaseous cobalt precursor up to surface saturation and c) removal of the remaining ligands by calcination in the synthetic air. Steps (b) and (c) were followed by a nitrogen purge. The cobalt content of the catalysts was increased by repeating steps (b) and (c).

2.5.2. Reverse micelle method

Reverse micelle method [48-49], as a kind of soft technique was used for obtaining the uniform and size controllable nanoparticles. The droplet dimension can be modulated by various parameters, in particular ($W = [\text{water}]/[\text{surfactant}]$). Several reverse micelle systems, especially AOT ternary water-in-oil system, have been used for preparing nanoparticles. Recent studies indicated that with the assistance of co-surfactant, the size of nanoparticles prepared in a quaternary reverse micelle system is more controllable. The reversed micelles containing micro droplets of aqueous FeSO were prepared by T. Kinoshita *et al.* [48] in an *n*-octane bath by mixing it with cetyltrimethylammonium bromide (CTAB) and 1-butanol as a surfactant and a co-surfactant, respectively. Firstly, FeSO in the reversed micelles was reduced by addition of aqueous sodium borohydride (NaBH₄) under

agitation with an ultrasonic homogenizer to obtain a colloidal dispersion of metallic iron. Secondly, an aqueous solution of HAuCl₄ was added to the solution. Then Au³⁺ was reduced by the same reducing agent. During the procedure, the reaction temperature was kept at 303 K, and argon gas bubbles were produced in the micelle solution to purge the oxidizing atmosphere. The products were then dried under vacuum, and the surfactant was rinsed off to obtain a powder sample.

2.5.3. Modified reverse-phase microemulsion method

Firstly, two kinds of solution (solutions A and B) are prepared [50]. Solution A is composed of 15.05 g of NP-7, 35.05 g of cyclohexane, and 8.05 g of *n*-butyl alcohol. Solution B is obtained with the addition of 2.00 g of NH₃·H₂O (16 %) to the cobalt acetate aqueous solution (0.13 g of Co(OAc)₂·4H₂O and 5.35 g of deionized H₂O). Microemulsion is obtained by the blending of solutions A and B. After stirring for 15 min 5.2 g of TEOS is added slowly to this microemulsion under stirring. After stirring for 12 h, 10 ml of acetone is added to destroy the microemulsion. Then it is centrifugated, washed with hot ethanol three times, and dried at 353 K for 12 h. This material is denoted as Co-SiO₂; scanning rate is 5°/min.

2.5.4. Gas-phase grafting method

Catalyst prepared by the gas phase grafting method [51] was in the reactor type equipment where the pressure can be reduced to the minimum of 0.1 Pa. The low pressure was used for removing physically adsorbed water at the temperature of 473 K for 4 h. The catalyst was further treated with oxygen at 2.7 kPa and 473 K for 30 min to remove organic residue and to oxidize the surface. The precursor was heated to a fixed temperature of 306 K to gradually evaporate a measured amount. The precursor was adsorbed on the metal oxide supports that were mounted in the reaction vessel and calcined in the air at fixed temperature in the range of 473–773 K to decompose into metallic gold particles on the support surface.

2.5.5. Liquid phase grafting method

Liquid phase grafting (LG) method [52] is used for depositing gold on several metal oxide supports such as TiO₂, Al₂O₃, SiO₂, *etc.* A weighted amount of the metal oxide support was introduced into an aqueous solution of HAuCl₄, Me₂Au(acac) and acetone. The mixture was kept in a refrigerator overnight and finally this solvent and metal oxide were separated by filtration and the metal oxide with the gold absorbed precursor which was calcined in the air at 673 K.

2.5.6. Co-sputtering and position

Columnar-structured porous films of Co_3O_4 were prepared on glass substrates by the oblique deposition of sputtered species emitted from a disk target of Co_3O_4 in a magnetron sputtering equipment [53]. During deposition the glass substrate was kept heated at 523 K and was rotated at 15 rpm. The distance between the target and the substrate was about 130 mm and the incident angle of the sputtered species against the substrate was about 45° . The content of Au in the films depends on the area of Au plate fixed on Co_3O_4 target. As an advanced modification, simultaneous co-sputtering deposition was also conducted to prepare Au/ Co_3O_4 films.

2.5.7. Alternative methods for preparation of gold nanoparticles

Titania Degussa P25 was used as the support and solid $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ – as the gold precursor [54]. Before preparation TiO_2 was previously dried in the air at 373 K for at least 24 h. All of the preparations were performed in the absence of light, which is known to decompose the gold precursors. 1 g of TiO_2 was added to 100 ml of an

aqueous solution of gold precursor. The amount of gold in the solution corresponds to a maximum gold loading of 8 wt % on TiO_2 . After deposition of gold onto TiO_2 it was followed by: (i) separation from the precursor solution by means of centrifugation (12 000 rpm for 10 min); (ii) washing (the solids were suspended in water (100 ml/g), stirred for 10 min at RT, and centrifuged again. This washing procedure was repeated four times to remove residual Cl^- and Na^+ ions as well as Au species not integrating the support); (iii) drying under vacuum at 373 K for 2 h; (iv) calcination at 573 K (300 mg of sample was heated in a flow. Calcination treatment leads to the decomposition of Au(III) complexes into gold metal particles); (v) storage of the samples away from light and under vacuum in a desiccator at RT. Indeed, a strong increase in the average particle size of the calcined samples was observed when samples are stored in the air even for a short period (for instance, from 1.8 to 3 nm for a sample left in the air for about 10 days). After several months of storage away from light in a desiccator, the average particle size also slightly increases (for instance, from 1.7 to 2.1 nm after 10 months of storage). To avoid this effect, the samples were stored after drying, and calcination was performed when needed.

Table

Recent literature review on cobalt catalyst for CO oxidation reactions

No.	Catalyst, prep. method	Exp. operating parameter	Remark	Ref.
1	2	3	4	5
1	Co promoted Pd, intermittently impregnating, calc. temp. 773–823 K	Horizontal quartz tube reactor, XRD, SET, and TEM	Different samples of the catalyst are prepared by varying cobalt and palladium content. The activity of these samples is described	[44]
2	Co, Ce promoted Pt and Pd, Pt and Pd applied by impregnation method, calc. at 823 K	Quartz-tube flow reactor, XPS, and BET, 1.0 % CO , 0.15 % C_3H_6 and 1.38 % O_2 , balanced with N_2 , space velocity (SV) of $90\,000\text{ h}^{-1}$ (NTP)	8 different samples were prepared by varying the composition of Pt and Pd. The catalytic activity of Pt is promoted by Co oxide in both lean and rich reactant gas, but CoO_x does not promote the activity of Pd	[55]
3	Pt and Co Oxide, impregnation method	Quartz flow reactor, 1.0 mol % CO and 0.6 mol % O_2 , at the flow rate of 200 ml/min	$\text{Pt}/\text{Al}_2\text{O}_3$, $\text{CoO}_x/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ are prepared to oxidise CO. This low-temperature activity of the cobalt containing catalysts was found to be independent of the presence of platinum	[56]
4	$\text{Au}/\text{MO}_x/\text{Al}_2\text{O}_3$, homogeneous deposition precipitation method, calc. temp 673 K	Fixed-bed reactor, 2 % CO and 2 % O_2 in He for CO oxidation, flow rate of 30 ml min^{-1}	The addition of transition metal oxides to $\text{Au}/\text{Al}_2\text{O}_3$ improves the catalytic activity in low temperature(250 K) of CO. Measured activities in CH_4 oxidation over $\text{Au}/\text{MO}_x/\text{Al}_2\text{O}_3$ decrease in the following order: $\text{CuO}_x > \text{MnO}_x > \text{CrO}_x > \text{FeO}_x > \text{CoO}_x > \text{NiO}_x > \text{ZnO}_x$	[29]
5	Ag-based composite oxides, co-precipitation method, calc. temp. b/w 473 to 773 K	25 mg, fixed bed quartz tube reactor, 1% CO in the air, $\text{SV} = 45000\text{ h}^{-1}$	1:1 molar ratio of Ag/Co and 1: 1 molar ratio of Ag/Mn calc. in air at 473 K for 3 h further proposed for the selective oxidation of carbon monoxide. 1: 1 molar ratio of Ag/Co composite oxide catalyst showed 90% of CO conversion at 453 K	[57]

Table (continued)

1	2	3	4	5
6	Supported Au catalysts, different methods of preparation	Mechanism for CO oxidation, deactivation and regeneration are discussed in respect to the available data	Data from diff labs are collected and the mechanism is developed for them. Effect of water and chlorides on the activity of the catalyst was also discussed	[58]
7	Supported gold catalysts Au/SiO ₂ , Au/Al ₂ O ₃ , Au/TiO ₂ by the gas phase grafting, calc. temp. of 673 K	100 mg, fixed-bed flow reactor, 1 % CO in the air or 1 % H ₂ in air flow rate of 33 ml/min. SV = 20000 h ⁻¹ ml/g catalyst	Gold deposited on SiO ₂ , Au/SiO ₂ -Al ₂ O ₃ , and Au/AC as nanoparticles has the high dispersion by the gas-phase grafting than by liquid-phase preparation methods	[51]
8	Co oxides, precipitation-oxidation method	In-situ FTIR study of cobalt oxide in a fixed-bed reactor is done	The characterizations of the cobalt oxides using TPR and XRD reveals that (i) the reduction of CoO _x in TPR proceeds in consecutive steps; and (ii) the variation in oxidation of CO is interpreted with a mechanism of oxygen species	[59]
9	Ce-supported Co, coprecipitation, impregnation methods	Fixed-bed flow system, two gas flow compositions were used: (i) 6 % O ₂ ; and (ii) 0.5 % NO + 6% O ₂ , the balance being helium	All the soot has been combusted by 673 K. Cobalt supported on alumina, silica, and tin oxide show much lower activity due to the presence of dispersed Co ²⁺ ions in these materials. This is due to the strong Co-support interaction, cobalt remains as dispersed Co ²⁺ ions and aggregation to form Co ₃ O ₄ microcrystallites occur only at more elevated temperatures	[60]
10	CoO _x /CeO ₂ catalyst, wet impregnation method calc. at 923 K	Quartz reactor, 1 % CO and 0.5 % O ₂ in N ₂ at space velocity of 30000 h ⁻¹	Different cobalt loading has been prepared and tested for CO oxidation in stoichiometric mixtures of CO and O ₂ and it was found that the finely dispersed CoO _x species that can absorb CO mainly contribute to the catalytic activity	[61]
11	CoO _x /CeO ₂ , co-precipitation method. Calc. temp. 923 K	0.1 g, quartz reactor, 1 % CO and 0.5% O ₂ in N ₂ , SV = 30000 h ⁻¹	Cobalt loading of 15 % on ceria can lead to the better dispersion of cobalt oxide	[62]
12	Co ₃ O ₄ , formed by heating a basic cobalt(II) carbonate precursor, calc. temp. 523 K	Characterisation of the catalyst is done by BET surface area analysis, powder X-ray diffraction	Catalyst formed by heating a basic cobalt (II) carbonate precursor in the air at 523–573 K shows much greater catalytic activity than Co ₃ O ₄ calc. at higher temperatures	[63]
13	Co ₃ O ₄ , precipitation method, calc. in the air at 1023 K for 20 h	The effect of the presence of humidity and molecular oxygen on the low temperature oxidation of the carbon monoxide on Co ₃ O ₄ powder surface was studied	The oxidation reaction is greatly enhanced by temperature: carbon dioxide forms significantly at T ≥ 323 K. The presence of humidity significantly decreases the conversion of CO to CO ₂ and facilitates the formation of carbonates	[64]
14	Pt-Co-Al aerogel catalysts, sol-gel method, calc. temp. 773 K	Fixed-bed micro reactor, H ₂ = 10000 ppm, CO = 1000 ppm, O ₂ = 1000 ppm, and N ₂ balance, SV = 6600–44000 h ⁻¹	Comparison of the catalysts are done by preparation methods and was found that the catalysts prepared by the sol-gel method show larger promoting effect of the cobalt addition than the catalysts prepared by the conventional impregnation.	[65]
15	Cobaltic oxide, precipitation-oxidation, impregnation and hydrothermal methods, calc. b/w 673 to 773 K	0.5 g, continuous flow micro-reactor, 10 % O ₂ /He with 4 % CO/He at the rate of 20 ml/min	Different samples of the catalyst are prepared by varying cobalt. Activity of the catalysts was compared in terms of surface area and particle size	[66]
16	Cu-Zn oxide and ceria, coprecipitation technique, calc. temp. 723 K	100 mg, quartz tube reactor, 3.6 % CO–21 % O ₂ –Ar, Flow rate of 1 l/min, SV varies from 15000 to 150000 h ⁻¹	It was shown that aged CuO-ZnO catalyst containing 60 % CuO and 40 % ZnO is highly active for the complete oxidation of CO to CO ₂ at ambient temperature. The	[67]

Table (continued)

1	2	3	4	5
			catalytic activity of the co-precipitated CuO-ZnO can also be improved significantly by the addition of CeO ₂ during the precipitation without the aging process	
17	Cu-Mn, sol-gel method, calc. temp. 673 K	100 mg, fixed-bed flow reactor, flow rate of 30000 ml h ⁻¹ g ⁻¹ , 1 % CO, 4.88 % synthetic air, 20 vol % CO ₂ in hydrogen	The influence of composition and calcination temperature (<i>T_c</i>) on the catalytic activity was shown for the oxidation of CO copper manganese oxides. Catalyst calcined at 673 K and at composition of 20 % Cu showed maximum conversion (60 %) of CO	[68]
18	Cobalt catalysts(5 % as metal Co loading on SiO ₂ , Al ₂ O ₃ and TiO ₂), incipient wetness impregnation method, calc. in air at 673 K for 4 h	40 mg, continuous flow micro-reactor, 10 % O ₂ /He with 4 % CO/He	The activities of the catalysts are described in terms of adsorption of CO and CO ₂ molecules. The reaction between adsorbed CO and lattice oxygen of cobalt oxide while both strong adsorption of CO on TiO ₂ and CO ₂ on cobalt oxide leads to affect the activity	[69]
19	CoO _x /Al ₂ O ₃ deposition oxidation-precipitation method, calc. temp. 383 K	0.15 g, isothermal plug-flow reactor, flow rate of 4.4 l/h, SV = 22000 h ⁻¹	Very high activity of the catalyst towards ozone decomposition even at 233 K	[70]
20	Co/ZrO ₂ , impregnation, Calcinations temp 773 K	200 mg, fixed bed flow reactor, varying gas concentrations of (CO, O ₂ , He). Flow rate is 45 cm ³ /min and SV = 35000 h ⁻¹	100 % conversion of CO to CO ₂ could occur even at room temperature	[71]
21	Co/(ZrO ₂ , CeO ₂ , SiO ₂ , Al ₂ O ₃ , and TiO ₂) prepared by wet impregnation, calc. temp. of 773 K	100 mg, quartz U-tube reactor with flow rate of 50 ml/min having feed of 1 % O ₂ , 1 % CO and 60 % H ₂ in He	Co/ZrO ₂ catalyst had the highest CO oxidation conversion of 94 % at 448 K from the rest of supports	[72]
22	CoO _x /ZrO ₂ , incipient wetness, impregnation technique, calc. temp. 773 K	200 mg, fixed bed reactor, flow rate 50 cm ³ (STP)/min, 1 % CO, 1 % O ₂ , 60 % H ₂ , and balance He, SV = 39000 h ⁻¹	Increasing GHSV causes decrease in CO conversion and an increase in O ₂ selectivity to CO ₂	[73]
23	Nanocrystalline Co ₃ O ₄ , calc. at 473, 523, 573 or 673 K which is formed by heating a basic cobalt(II) carbonate precursor in air at 523–573 K	DSC, TGA, XRD, XPS, BET isotherms, DR/FT-IR spectrometry of the catalyst have been studied	In the proposed mechanism CO is adsorbed on Co atoms in a low oxidation state, presumably Co(II). The adsorbed CO interacts with an oxygen atom bonded to a neighbouring Co(III) atom in a strongly exothermic reaction, forming vibrationally excited CO ₂	[74]
24	Co promoted Cu-Mn oxide catalysts, co-precipitation, calc. temp. 688 K	Catalysts containing 0, 1 and 5 mol % Co were tested for the oxidation of CO in a fixed bed reactor, oxidation at 298 K using 5000 ppm CO in the air, SV = 33000h ⁻¹	Low levels of cobalt doping (1 wt %) of copper manganese oxide enhance its activity for carbon monoxide oxidation under ambient conditions	[75]
25	Mesoporous Co ₃ O ₄ -CeO ₂ and Pd/Co ₃ O ₄ -CeO ₂ , surfactant-template method, promoted by Pd (0.5 wt %), calc. temp. 773 K	600 mg, fixed-bed quartz tubular reactor, feed gas of 1 % CO, 5 % O ₂ -N ₂ , flow rate of 100 ml·min ⁻¹ ; SV = 10000 ml·g ⁻¹ ·h ⁻¹	Pd prominently enhances both the reduction and oxidation performance of the catalysts, due to hydrogen or oxygen spill over	[76]
26	CeO ₂ /Co ₃ O ₄ prepared by the impregnation method, calc. temp. 473 K	0.5 g, continuous flow micro-reactor, flow rate of 20 ml·min ⁻¹ contains 4 % CO/He	Ce20/R230, increased surface area of cobaltic oxide, 100 % conversion of Co was obtained at 443 K	[77]
27	Effect of Cu on alumina supported Au catalysts, deposition precipitation	200 mg, glass micro reactor, 1 % CO; 0.5–1.5 % O ₂ ; 30 % H ₂ ; 0–30 % CO ₂ ; 0–10 % H ₂ O	Interaction between Cu and Au seemed to be able to modify the catalytic properties of Au active sites for CO oxidation. 100 %	[24]

Table (continued)

1	2	3	4	5
	method, calc. temp. 773 K	and He balance, flow rate 100 ml·min ⁻¹	conversion was achieved with 2.5 % Au–0.5 % Cu/Al ₂ O ₃ at 323 K	
28	Gold nanoparticle	The glass reactor was used for the study of the catalyst by varying the total surface area of a gold catalyst: 3.36, 18.48, 33.6 m ² ; CO gas concentration: 10 %, 30 %, 50 %; relative humidity: 9 %, 50 %, 100 % respectively.	The results indicate that the conversion efficiency of CO was high when the ratio of CO and O ₂ was close to 1:1. The gas concentration is the most important factor, followed by the weight of gold catalyst, followed by the relative humidity	[78]
29	Cu-Mn oxide, redox method, calc. temp. 573 K	100 mg, quartz tubular fixed bed flow reactor, 1 % CO, 2 % O ₂ and 5 % N ₂ in He. SV=12000–35000 ml·h ⁻¹ ·g _{cat} ⁻¹	The catalytic performance of catalysts prepared using the redox method compared with a commercial Hopcalite catalyst. The optimum copper loading was determined to be 9 % of the manganese content at ambient temperature	[79]
30	Cu-Mn oxide modified by Au, co-precipitation method, calc. temp. 688 K	Fixed bed micro reactor, space velocity of 12000 h ⁻¹ , flow rate of 15 ml·min ⁻¹	The addition of Au to an active hopcalite catalyst, using a deposition-precipitation procedure, leads to a marked improvement in activity towards CO oxidation	[80]
31	Co/CeO ₂ nanoparticles, incipient wetness impregnation, calc. at 673 K	100-200mg, 1 % CO, 1 % O ₂ , 10 % H ₂ and balance helium. Characterisation done by TEM, LRS etc.	Oxidation was done at three temperatures and it was found that below 448 K, CO oxidation is dominant between 448 and 548 K, CO oxidation competes with H ₂ combustion and above 548 K, methanation dominates. The high-surface area 10 % CoO _x /CeO ₂ catalyst is highly effective for the preferential oxidation of CO in H ₂ rich feed	[81]
32	Cu-Mn oxides, redox method, calc. temp. 573 K	100 mg, continuous flow fixed bed quartz tubular reactor, 1 % CO, 1 % O ₂ , 60 % H ₂ balanced with N ₂	Catalyst having the copper/manganese ratio of 0.06 shows the maximum conversion at 323 K. The high catalytic activity was attributed to a combination of factors including the high surface areas, low crystallinity, compositional homogeneity, low activation energy, and the presence of readily available lattice oxygen for CO oxidation	[82]
33	CoO _x /γ-Al ₂ O ₃ , wet impregnation, calc. temp. 1023 K	50 mg, microreactor, 1.6 % CO, 20.8 % O ₂ , and 77.6 % N ₂ ; SV = 72000 ml/g·h	CoO/γ-Al ₂ O ₃ loaded with 61.2 mmol/(100 m ² γ-Al ₂ O ₃) is more active than Co ₃ O ₄ /γ-Al ₂ O ₃ catalysts for CO oxidation	[83]
34	CoO _x /CeO ₂ , wet impregnation method, calc. temp. 673 K	50 mg, fixed bed reactor, flow rate 130 cm ³ /min, 2 % CO, 2 % O ₂ , balance He, SV = 15000 cm ³ ·(g cat ⁻¹)·h ⁻¹	Higher Co loadings favoured CO oxidation at low temp. (T ≤ 423 K) under dry conditions	[84]
35	Nanosized Fe–Co mixed oxide prepared by co-precipitation method, calc. temp. 673, 773 and 873 K for 4 h in air	100 mg, bed quartz micro-reactor, 2 % CO, 20 % O ₂ and 10 % N ₂ balanced with He, GHSV of 60000 ml/g·h	Addition of Co to iron oxide causes an increase in CO conversion. Results indicate that calc. at lower temperatures and/or introducing oxidative pretreatment has an extensive role to increasing activity of CO oxidation on Fe–Co mixed oxide catalysts	[85]
36	Co/Al ₂ O ₃ , impregnation and sol-gel, 623 K	200 mg, tubular flow reactor, 8 ml/min CO and 4 ml/min O ₂ , which was balanced with He to a total flow rate of 50 ml/min	Catalyst prepared by impregnation methods has the high activity.	[25]
37	Co ₃ O ₄ /Al ₂ O ₃ , precipitation method, calc. at 823 K	Vertical quartz tube reactor, 6 vol % O ₂ /argon gas mixture	The preoxidised catalyst shows the higher activity for CO oxidation than the prereduced catalyst	[26]

Table (continued)

1	2	3	4	5
38	Co/Al ₂ O ₃ , deposition-precipitation, incipient-wetness impregnation, oxidative decomposition, calc. at 623 and 773 K, respectively	0.5 g, quartz U-tube microreactor, 100 ml/min of 0.095 % NO, 0.1 % C ₃ H ₆ , 5 % O ₂ , and 1.7 % H ₂ O, balanced with He	Co/Al ₂ O ₃ catalysts have been found to be active and stable in NO SCR reaction	[86]
39	Co/Al ₂ O ₃ , impregnation method, calc. temp. 1373 K	0.3 g, U-shaped quartz glass reactor, 750 ppm of NO, 680 ppm C ₃ H ₆ , 4 % O ₂ and the rest was N ₂	Co/Al ₂ O ₃ has the high performance prepared by sol-gel than impregnation	[87]
40	CoO _x catalysts, sol-gel method, calc. temp. 923 K	100 mg, fixed bed flow reactor, 1000 ppm of NO, 1000 ppm of C ₃ H ₆ , 5 vol % O ₂ , balance He	CoO _x /Al ₂ O ₃ -BaO catalysts are more stable and more active in NO SCR, than the corresponding ones supported on alumina	[88]
41	CoO/γ-Al ₂ O ₃ , deposition precipitation, calc. temp. 923 K	200 mg, continuous flow fixed-bed microreactor, 0.1 % v/v NO, 0.1 % v/v C ₃ H ₆ , 10 % O ₂ with N ₂ as balance	The increase of Co loading over 5 % favoured the formation of supported Co(III) oxospecies on the support surface	[89]
42	Co-based alumina catalysts, co-precipitation, 1073 K	0.5 g, fixed-bed stainless steel reactor, 1000 ppm NO, 1000 ppm C ₃ H ₈ or C ₃ H ₆ , 5 % O ₂ , and He	Effect of additive metals can be described as follows: CoZn > CoAg, CoNi > CoCu > CoFe. Maximum NO conversion of 96 % was achieved at the reaction temperatures of 723 K on 8Co4ZnA800 sample	[90]
43	CoO _x /Al ₂ O ₃ , co-precipitation, sol-gel, incipient wetness impregnation and solid dispersion, calc. temp. 723 K	Continuous flow fixed-bed microreactor, 1000 ppm NO, 1000 ppm C ₃ H ₈ and 10 % O ₂ , helium as balance gas, GHSV = 10000 h ⁻¹	The optimized CoO _x /Al ₂ O ₃ catalysts have been found to be active in SCR of NO by C ₃ H ₈ . The SCR activity increases with an increase in the strength of cobalt-alumina interactions in the catalysts	[91]
44	CoO/Al ₂ O ₃ , FeO/Al ₂ O ₃ , impregnation, sol-gel method, calc. temp. 873 K	0.2 g, fixed bed flow reactor, NO, NO ₂ , O ₂ and C ₃ H ₆ diluted in helium; flow rate is 62 cm ³ /min	Cobalt/aluminate species are much more stable than iron/aluminate	[92]
45	Co-Beta, calc. temp. 823 K	4 ml, fixed-bed flow reactor	Highly-dispersed cobalt is essential for the high activity and selectivity for NO _x reduction	[93]
46	Co ₃ O ₄ /γ-Al ₂ O ₃ , combination of wetness impregnation and subsequent combustion, calc. temp. 873 K	1.0 ml, quartz tubular fixed-bed reactor, space velocity of about 15000 h ⁻¹	Combustion-synthesized Co ₃ O ₄ /γ-Al ₂ O ₃ catalysts retained better activity than the catalyst prepared by the thermal decomposition of cobalt nitrate	[94]
47	Cobalt/alumina, impregnation, calc. temp. 573 K	50 mg, continuous flow fixed-bed micro-reactor, 250 ppm C ₆ H ₆ , 20 % O ₂ with nitrogen as a balance	It was found that two parameters influence the catalytic activity; the dispersion and the characteristics of the 'active species'	[95]
48	Cobalt oxide, wet impregnation method, calc. temp. 773 K	250 mg, fixed bed quartz reactor tube, 8000 ppm propane in air with a total flow rate of 50 ml/min	Total conversion has been attained at a reaction temperature as low as 523 K	[96]
49	Ce-Pt/Al ₂ O ₃ , sol-gel method, calc. temp. 673 K	140 mg, tubular fixed bed reactor, 19.38 % of O ₂ , 77.52 % of N ₂ , 3 % of H ₂ O and 0.1 % of VOC	Results reveal that the presence of ceria affects the reducibility of the material surface, show an increase of the oxygen storage capacity when increasing the ceria loading	[97]
50	Pt, Pd and Pt+Pd/γ-Al ₂ O ₃ and on TiO ₂ , impregnation method, calc. temp. 593 K	Stainless steel tube reactor, GHSV = 21000 h ⁻¹	Pd/Al ₂ O ₃ is a superior catalyst and has shown the higher activity towards methane combustion	[98]
51	Pt catalysts, impregnation method, calc. temp. 873 K	20–60 mg, quartz reactor, 250 ppm VOC, SV = 30000–400000 h ⁻¹	Pt for benzene and ethylacetate oxidation is enhanced, when it is supported on TiO carriers doped with W ⁶⁺ cations	[99]

As seen from the Table, extensive amount of work has been done on cobalt catalyst. Oxidation is not the only field where it has been studied but there are other promising fields where it has been explored such as medicine [100-103], Fischer-Tropsch synthesis [104-105], pharmaceutical industry [106-107], food [108-109], agriculture [110-111]. Besides the exploration of cobalt in many fields it is also regarded as cheap or economical [112] and easily available compound. Recently cobalt has been reported for oxidation studies [113-118], cobalt oxide [119-120] catalyst due to its unique activity for CO oxidation. Past experience also revealed that the oxidation activity of these base metal oxide catalysts can be prominently enhanced by the several metal oxides such as ceria [72], zirconium dioxide, silicon dioxide, aluminium dioxide, titanium dioxide [51], gold [57], copper manganese oxide [23]. Nowadays, more and more studies are focusing on the catalysts with the combination of noble metal and base metal oxides for oxidation applications [80, 27]. It has also been shown that calcinations in the presence of oxygen yields a highly reactive catalyst for the room temperature oxidation of CO with observed light-off temperature as low as 210 K [56, 121]. C.-B. Wang and his co-workers have done considerable amount of work on cobalt as a catalyst for the oxidation of carbon monoxide. Different supports are being used and characterised for the betterment of the catalyst, *i.e.* for the conversion of CO. With the increase in the oxidation state of cobalt, the activity of the catalyst decreases [59]. Again in 2005, different methods of catalyst preparation were adopted and hence correlations between a catalytic activity and surface area properties are obtained. It was concluded that pre-treatment of the catalyst with H₂ can reduce the conversion temperature [66]. Different supports, *i.e.* 5 % as the metal Co loading on SiO₂, Al₂O₃ and TiO₂ were studied and their catalytic activities were tested. Co/SiO₂ showed 100 % conversion at 453 K followed by 95 % for Co/Al₂O₃ and 25 % for Co/TiO₂ [56]. Other transition methods [21, 52, 59, 63, 66, 69, 77] were also studied by varying their compositions. Review of copper chromite catalysts for CO oxidation [45, 83] published a review article on VOCs. Hence their effects have been studied accordingly. Catalysts of different composition with ceria have been prepared and characterised. According to the results, the optimum loading of ceria is 20 %. It exhibits the highest surface area and the best catalytic activity toward CO oxidation ($T_{50\%} = 361$ K) among those catalysts [77].

3. Conclusions

On the basis of the above study that was made primarily on carbon monoxide with many other hazardous

materials as well, we can sum up the results. We have enough spoken about various parameters such as sources of the pollutants, their causes, their effects on humans and things and at the end we described the removal of these compounds by the uses of different catalyst. The catalysts that are used in a catalytic converter by most of the manufactures till date are the noble metals. However, the high cost, their sensitivity to sulphur poisoning and limited availability of the precious metals have encouraged researchers to look for alternative catalysts. In the last decade much attention has been paid to the base metals, *i.e.* due to their higher thermal stability, environmentally friendly properties and lower price, transition metal oxides are suitable alternative for the precious metals. They are less active at low temperatures, but at higher temperatures their activity is similar to that of the noble metals. Many review articles were published keeping in view literature accumulated. Cobalt has been reported and regarded as a good catalyst from economical, thermal stability, activity, selectivity and availability point of view. These properties make it a good catalyst in comparison to other base metal catalysts. Various mechanisms are also proposed in view of CO oxidation reaction on cobalt based catalysts. These mechanisms are reliable and good enough as per current co-relations present in the literature.

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ОКИСНЕННЯ МОНОКСИДУ ВУГЛЕЦЮ З ВИКОРИСТАННЯМ КОБАЛЬТОВИХ КАТАЛІЗАТОРІВ: КОРОТКИЙ ОГЛЯД

Анотація: Розглянуто методи приготування і основні характеристики відомих каталізаторів для окиснення монооксида вуглецю. В таблицній формі приведено короткий огляд літератури основних металовмісних каталізаторів (головним чином, кобальтових) для реакцій окиснення CO.

Ключові слова: кобальт, каталізатор, монооксид вуглецю, каталітичний конвертор, автомобільні вихлопи.