Critical Review of Low-Temperature CO Oxidation and Hysteresis Phenomenon on Heterogeneous Catalysts

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Abstract: There is a growing demand for new heterogeneous catalysts for cost-effective catalysis. Currently, the hysteresis phenomenon during low-temperature CO oxidation is an important topic in heterogeneous catalysis. Hysteresis provides important information about fluctuating reaction conditions that affect the regeneration of active sites and indicate the restoration of catalyst activity. Understanding its dynamic behavior, such as hysteresis and self-sustained kinetic oscillations, during CO oxidation, is crucial for the development of cost-effective, stable and long-lasting catalysts. Hysteresis during CO oxidation has a direct influence on many industrial processes and its understanding can be beneficial to a broad range of applications, including long-life CO₂ lasers, gas masks, catalytic converters, sensors, indoor air quality, etc. This review considers the most recent reported advancements in the field of hysteresis behavior during CO oxidation which shed light on the origin of this phenomenon and the parameters that influence the type, shape, and width of the conversion of the hysteresis curves.

Keywords: CO hysteresis; self-Sustaining CO oxidation; dynamic catalysis; catalytic activity; catalyst; Isothermal; bi-stability region

1. Introduction

Carbon monoxide (CO) is a toxic gas that is often called the silent killer since it does not have taste, color or smell and generally results from incomplete combustion of fossil fuels. Most of the CO emission occurs due to cold start of vehicles [1–5]. A small exposure to CO can be fatal since it has a high affinity to replace oxygen and binds to hemoglobin in blood cells [6].

Catalytic CO oxidation has gained increasing attention in recent years, primarily due to its demand in industrial processes, such as: pollution reduction in the auto industry, abatement of gaseous waste in petrochemical industries, synthesis of pure gases, ethanol or other fuel production, and pure hydrogen production for proton-exchange membrane fuel cells [7–9]. CO oxidation also has a wide range of diverse applications in long-life carbon dioxide (CO₂) lasers, gas masks, catalytic converters, sensors, indoor air quality improvement, etc. [10–13]. Catalytic CO oxidation has been widely studied, especially for application in automotive industry [14–16]. High operation temperature (>570 K) of the widely uses three-way catalytic converters inhibit the conversion of CO and other pollutants during the cold start period. Hence, recent studies have targeted the development of new cost-effective and low-temperature catalysts [17–19].

The CO oxidation reaction is one of the most extensively studied in the history of heterogeneous catalysis. Often, CO oxidation is considered to be an interesting probe reaction for other oxidation
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reactions and is an essential reaction for cleaning air and lowering automotive emissions as reported in the web of science database, and the publications on this subject are growing exponentially [20].

Transition metals are widely used to activate surface catalyzed reactions, such as CO oxidation, primarily due to high dissociation probability and very low adsorption energy. Transition metals are characterized by their half-filled d-bands which enables them to have the highest activity compared to other metals. Thus, platinum group metals, such as platinum (Pt), palladium (Pd) and rhodium (Rh), are considered the most efficient transition metal catalysts. They have emerged as most efficient catalysts due to their ability to dissociate molecular oxygen at a low temperature and to bind strongly with both atomic oxygen and CO [21]. Noble metal catalysts are known for their excellent activities, such as water tolerance, and low light-off temperatures [22,23]. Recent studies report that gold (Au) is highly active towards CO oxidation at low temperatures (close to ambient temperature) [24–28] even though single molecule CO conversion are prohibited due to the presence of water [29]. Gold’s selective binding to CO and non-selective loose binding to other reactants causes its high activity which may provide sufficient concentration of CO on surfaces, thus lowering the activation energy to a negligible value enabling the reaction to proceed at room temperature [30]. The high activity of gold towards CO oxidation is reported to be maximum for gold particles (<5 nm in size) supported on reducible metal oxides, such as ceria [24], iron oxide, or titania [25,31–36]. CO oxidation reaction with gold catalysts occur at the interface between the gold metal particle and the oxide support, the CO adsorbed on the gold particles and oxygen (O₂) activated from the oxide support [31,33,34,37–39].

Recent studies focus on reducing the high cost of noble metals and improving the stability of catalysts, motivating the investigation for new materials such as Mn, Fe, Co, Ni, Cu or their combinations and concepts to reduce the use of precious metal content to find suitable substitutes for noble metals [40–45]. As the high activity, high selectivity, and long lifetime of the catalysts are a challenge in heterogeneous catalysis, it is crucial to design catalysts with active sites and other features, to render them useful for any specific applications. Although CO oxidation in the presence of O₂ is considered a relatively simple reaction, researchers have proposed over 20 different mechanistic steps occurring during this reaction [46–53]. One of the most acceptable mechanisms for low-temperature CO oxidation is the Langumir–Hinshelwood (LH) dual-site mechanism, in which the reaction is considered to occur between CO and O₂ after both molecules have been adsorbed on the surface of a catalyst [52,54,55]. One of the most challenging tasks in heterogeneous catalysis is understanding catalysts under conditions of dynamic reaction and investigating the microscopic processes occurring at the surfaces and in the bulk material of solid catalysts during both heating and cooling cycles [56].

CO oxidation has received a great amount of attention in studies on catalytic reaction dynamics due to its rich, dynamic behavior, wherein it exhibits hysteresis behavior, i.e., regions where multiple steady states are observed for a broad range of experimental conditions, such as dynamic behavior with kinetic instabilities, hysteresis effects and self-sustained oscillations [57]. This review highlights the importance of understanding the dynamic behavior of catalytic oxidation of CO for the future development of catalytic CO oxidation systems.

2. Origin of Hysteresis Phenomenon in Low-Temperature CO Oxidation

Hysteresis is defined as the dependence of the state of a system on its history. Hysteresis occurs in many systems, such as in ferromagnetic and ferroelectric systems, as well as in catalytic materials. Hysteresis effects can be a dynamic lag between an input and an output which disappears if the input is varied very slowly; this is often known as rate-dependent hysteresis [58]. This type of hysteresis has a persistent memory of the past state that persists after the transients have died out [59,60]. Adsorption hysteresis is one of the well-known hysteresis that occurs during physical adsorption processes where the quantity adsorbed is different when the gas is being added than when it is being removed. This hysteresis is caused by the differences in the nucleation and evaporation mechanisms inside mesopores, and can be related to other effects, such as cavitation and pore blocking. This effect
was reported in physical adsorption, where hysteresis was influenced by mesopores (2–50 nm) which is associated with the appearance (50 nm) and disappearance (2 nm) of mesoporosity in nitrogen adsorption isotherms as a function of Kelvin radius [61]. Furthermore, the effect of the support during the thermal decomposition hysteresis of palladium oxide (PdO) supported on zirconia (ZrO$_2$), titania (TiO$_2$), ceria (CeO$_2$), and gamma-alumina ($\gamma$-Al$_2$O$_3$) was observed and investigated by Farrauto et al. who reported large hysteresis width in thermal resistance of $\gamma$-Al$_2$O$_3$ followed by ZrO$_2$, and relatively small hysteresis for TiO$_2$ and CeO$_2$, respectively [62].

In heterogeneous catalysis, often temperature hysteresis is observed when the reaction parameter during a complete cycle, such as reaction rate or the degree of conversion, does not match with increasing and decreasing temperatures. As a consequence, a hysteresis loop is created, where the ascending and the descending branches of the conversion (%) vs. temperature plot do not coincide. Hysteresis can also be explained based on the existence of several steady states in a catalytic systems, where, during a gradual temperature change, one steady state is replaced by another state with different kinetic features, reacting to proceed at a different rate for constant reactor temperatures [63–65].

The hysteresis behavior of CO oxidation over Pd/SiO$_2$ and (Pd + Cr$_2$O$_3$)/Al$_2$O$_3$ catalysts has been studied experimentally and explained based on the existence of different steady states during reaction [65]. Recent CO oxidation studies during heating followed by cooling cycles have shown hysteresis behavior, with higher conversions during extinction [5,49,52,56,66–73]. Yap et al. described that the ignition-extinction hysteresis occur following the steps listed herein: (1) adsorption of CO at low temperatures; (2) ignition when CO starts to desorb from a catalyst surface; (3) CO and O adsorption on the active sites and surface reactions take place between adsorbed CO and O; (4) trigger an increase in the reaction rate; (5) stability during high reactive state and a balance between heat generation and the heat losses; (6) interaction of the CO more strongly with the surplus oxygen allowed by the oxygen covered surface at high temperatures which enhances reactivity by lowering activation energy; (7) high and stable reaction rate due to the enhanced reactivity between adsorbed CO and the high oxygen coverage as the catalyst temperature drops which gives rise to a hysteresis phenomenon or having two values of reaction rates at the same temperature [74].

During ignition (light-off) and extinction (light-out) exothermic CO oxidation reactions, hysteresis can occur during the conversion as a function of temperature. Consequently, a hysteresis loop can appear because of a mismatch between the activity during the ignition and extinction processes. There are three regions of activity observed: the first region has low activity (before the light-off temperature), where CO is adsorbed on a catalyst surface, followed by a region with high activity at a higher temperature (after the light-off temperature) and finally, a region of bi-stability before the light-out temperature, as shown in Figure 1.

Hysteresis effects in CO oxidation [75,76], as well as methane oxidation reactions, have been reported [77–80]. Several studies report the differences in the activity of CO, NO, C$_3$H$_6$, and CH$_4$ oxidation on Pt and Pd catalysts during the light-off and the light-out [67,77,81–83]. A typical hysteresis behavior for CO oxidation over Pt/Al$_2$O$_3$ has been extensively studied and reported [49,53,55,56,84–90]. Simultaneous oxidation of CO and CH$_4$ on Pt/Al$_2$O$_3$ and Pt/CeO$_2$ results in a reverse hysteresis for methane oxidation [5]. Moreover, CO self-sustained combustion over the Cu-Ce/ZSM-5 or CuCe$_{1–x}$Zr$_x$O$_y$/ZSM-5 catalyst has been reported [91,92]. The explanation of hysteresis effects by multiple steady states has been comprehensively reviewed by Hlaváček et al. [93]. Engel et al. have explained the appearance of a hysteresis loop in CO oxidation on a contaminated platinum wire by removing sulfur and carbon impurities which could affect the reaction on the metal surface [75]. A higher conversion often indicates normal hysteresis behavior during extinction. The higher activity of the catalyst during extinction can be attributed to surface inhibition by CO adsorption, reaction exothermicity, and thermal inertia of the catalyst. Carlsson et al. [5], argued that normal hysteresis occurs due to three possible reasons: (1) kinetic bistability, (2) interaction between reaction kinetics and diffusion phenomenon, and (3) local overheating of catalyst surfaces.
CO inverse hysteresis behavior was observed in the case of gas mixtures, such as CO, nitrous oxide (NO) and propane (C₃H₈) mixture, where the catalytic activity during ignition exceeded the activity during extinction. The inverse hysteresis was theorized to occur due to high-temperature oxidation of Pt in the presence of NO or C₃H₈, to form an oxide phase that is less catalytically active than metallic Pt. Additionally, at low-temperatures, Pt oxide is reduced back to metallic Pt [67]. This behavior is observed for switching of CO hysteresis behavior from normal hysteresis to inverse hysteresis in a CO/NO/O₂ mixture, which was attributed to reversible oxidation of the Pt surface [67,91]. Inverse hysteresis is also observed for catalysts containing very small Pt- nanoparticles (<2 nm), while typical hysteresis is observed for large Pt- nanoparticles which could be attributed to the different CO adsorption strengths, surface-bulk oxidation of Pt particles, and regeneration of the active sites [94]. Normal hysteresis is observed for the PdCu(110) and Cu–Ce–Zr–O systems [90,95] single crystal alloys, while inverse hysteresis is observed on unsupported catalysts, such as Pd/Ag alloys [96]. Rapid CO adsorption and diffusion is considered crucial for producing strong hysteresis and bistability [97].

Beusch et al. first introduced isothermal multiplicity, such as hysteresis and oscillation in CO oxidation, on Pt-cylindrical catalyst pellets in 1972 [98]. It was argued that hysteresis was independent of the total volumetric flow rate and in-effect related to the multiplicity in the system and is influenced due to the reaction and the chemisorption rates. The results were explained to occur following the Eley–Rideal mechanism with oxygen reacting with adsorbed CO following Langmuir model for adsorption. Multiple steady states could occur when the intrinsic rates of the reaction and chemisorption steps are roughly of equal size [98]. However, theoretical studies suggest that a reactant concentration gradient occurs during reactions in LH models, wherein one of the reactants is strongly adsorbed, leading to isothermal multiplicity [99–101]. As a result, the multiplicity is explained by the interaction of intraparticle diffusion and surface reaction of a sorption step involving at least one strongly adsorbed reactant [99–101].

The hysteresis effects are mostly observed in the oxidation of CO in supported and unsupported metal catalysts [5,52,55,56,96]. Most studies focused on Pt or Pd catalysts supported on alumina [73,102–106] or silica [107,108] substrates. Other studies suggest that diffusion–reaction interactions can lead to multiplicity [69,70]. Eigenberger et al. showed that two or more surface rate steps of roughly equal magnitude could lead to isothermal multiplicity in a gradient-less reactor [109].

**Figure 1.** Typical hysteresis can occur during ignition (light-off) and extinction (light-out) exothermic CO oxidation reaction.
In 1978, Cutlip and Kenney were able to explain and revised Beusch’s hypothesis to explain their experimental observations [103]. Recent experimental observations suggest that the hysteresis during CO oxidation arises from the diffusion-reaction interaction. Hegedus et al. reported that the increase in the intrapellet diffusion resistances of supported metal catalyst (e.g., Pt/A120 catalyst), upon aging, leads to a significant broadening of the multiplicity region (hysteresis width) agreeing well with transport hypothesis, as suggested by Oh et al. [68]. Chakrabarty et al. explained hysteresis based on the surface reaction–sorption interferences, where sorption of the reactants on the catalyst surface is important to the obtained hysteresis behavior, leading to isothermal multiplicity [56]. Similar observations for multiplicity have been explained; they occur due to the competition of sorption by reactants [98,110,111] and switching of the type of CO complexation on catalyst surface [112] or the interaction of O2 with chemisorbed CO [113]. This phenomenon could be explained by the alternation between metallic Pt active species and surface-oxidized Pt nanoparticles (NPs). The local CO consumption can lead to the increase or decrease in CO conversion [114,115]. Similar results were reported for P(111) [116]. Subbotin reported that the value of the temperature hysteresis in CO oxidation on copper-cermet catalysts increase with increasing CuO content [117].

Although the hysteresis in CO oxidation over various catalysts have been reported in recent years, a majority of the authors did not propose any original interpretation of this phenomenon. Instead, they attribute the hysteresis phenomenon to the presence of multiple steady states as a necessary condition for hysteresis [114,115]. Frank-Kamenetski suggested the concept of temperature hysteresis in heterogeneous catalysis based on the macro-kinetic transition from the kinetic to the diffusion mode during hysteresis [118].

Recently, the hysteresis phenomenon was explained to arise due to the existence of some steady states in a catalytic system, phase transitions in catalysts, changes in the surface state of the adsorbed components, and removal of admixtures from a catalyst surface that can hinder the reaction. Subbotin et al. explained the hysteresis effect based on the exothermic heterogeneous catalytic reaction upon reaching a particular reaction rate; the amount of heat liberated at an active reaction center becomes too large to be dissipated in the environment [119,120]. Generally, this is due to the poor heat conductivity of porous oxide supports or poor active centers of inactive catalytic mass. As a result, the actual reaction temperature of the active center is higher than the average temperature of the catalyst bed, leading to local overheating of the active centers and thus a higher conversion than expected at the measured temperature. After the heating is turned off, the excessive heat requires a longer time to dissipate due to poor heat removal, maintaining an actual temperature of the active centers that are higher than the temperature measured by a thermocouple [119,120]. The local overheating of active sites as a result of the liberation of excessive heat during the highly exothermic reaction of the CO oxidation into CO2 leads to a catalyst remaining active at lower temperatures during extinction [71,121]. The formation of hysteresis loops in CO oxidation has also been attributed to CO island formation by some authors [30].

Kipnis explained the role of reaction exothermicity and nanometer-scale particle size of CO oxidation on supported Au- nanoparticles and explained the jump of conversion as a result of temperature variation, CO conversion hysteresis, appearance of a hot spot, and precursor self-activation because of sharp decrease in apparent activation energy of the catalyst and the exothermicity of CO oxidation which brings the reaction into an external diffusion control regime [122–124]. Similar results were reported for the hysteresis in preferential CO oxidation over a ceria-supported catalyst containing 0.28 wt% Au and germanium (Ge) and gadolinium (Gd) dopants which was attributed to catalyst activation [97]. It was reported that the “direction” of the hysteresis depended on the CO partial pressure [120,125].

3. Effect of Catalysts and Reaction Parameters/Conditions on Hysteresis Behavior

In a catalytic reactor, inlet temperature, gas pressure, particle size, type and nature, inlet gas composition and reactant concentration affect the performance of a catalyst [126]. Casapu et al.
investigated Pt particle size distribution on the hysteresis during CO oxidation over Pt/Al₂O₃ and found that hysteresis is strongly dependent on the particle size of the catalyst. Inverse hysteresis is observed for catalysts containing very small Pt-nanoparticles (< 2 nm), and normal hysteresis for large Pt-nanoparticles, which was attributed to the different surface/bulk CO adsorption strength, oxidation of Pt-nanoparticles, the catalyst active sites regeneration and the exothermicity of the CO oxidation reaction (Figure 2) [94].

![Inverse hysteresis and Normal hysteresis](image)

**Figure 2.** Light-off and light-out temperatures vs. average Pt particle size during CO oxidation [94].

The inlet gas stoichiometric ratio of CO and O₂ has also been investigated and recent data shows that it could affect the conversion profile and the dynamic behavior of a catalyst [127]. Newton reported that hysteresis effect is dependent on the ratio between O₂/CO during CO oxidation over Pt surfaces and supported catalysts, such as Pt/Al₂O₃, and the optimum ratio were (1 < O₂/CO < 5) [127].

Most of the reviewed literature reported the effect of CO concentrations at different inlet temperature on hysteresis behavior [77,128–134]. The width of the hysteresis loop was larger for higher CO concentrations, as shown in Figure 3.

![Temperature-programmed CO oxidation](image)

**Figure 3.** Temperature-programmed CO oxidation with the following inlet conditions: 1000 ppm or 500 ppm CO, 10% H₂O, 10% CO₂, and 10% O₂ over a Pt/Al₂O₃ monolith [77].
Subbotin et al. studied CO oxidation hysteresis behavior on Pt foil and CuO and found that the hysteresis is wider for the CuO catalysts, which could be attributed to the higher activity in CuO catalysts as compared to that on the Pt foil. Figure 4 shows the study of hysteresis phenomenon on unsupported CuO prepared by the decomposition of Cu hydroxycarbonate, which is one of the most active catalysts for this reaction on Pt-foil [63].

Figure 4. Hysteresis behavior during CO oxidation over unsupported copper oxide (CuO) (a) and over Pt foil (b) (the arrows mark the increase and the decrease in temperature) [63].

Carlsson et al. have studied oxidation of CO mixture in excess oxygen over Pt/Al2O3 and Pt/CeO2 catalysts with the platinum phase distributed either homogeneously or heterogeneously in the support material using temperature-programmed experiments [5]. It has been found that the hysteresis width increases with decreasing CO concentrations, and at 0.1% CO, hysteresis is significantly broader for the heterogeneously distributed platinum catalysts compared to the homogeneously distributed Pt catalysts, as shown in Figure 5.

Furthermore, they studied the effect of the support in case of Pt/CeO2 monolith catalysts. Results indicate that the width of the hysteresis does not change for CO concentrations, as shown in Figure 6 [5]. Lin et al. studied the hysteresis behavior of Pd/Al(OH)3 and Pd/Mg(OH)2 catalyst and found that Pd/Al(OH)3 catalysts have smaller hysteresis compared to Pd/Mg(OH)2 catalysts [135]. The porosity of catalyst support assumes a role in temperature hysteresis activity during CO oxidation reaction. For example, hysteresis was absent in Pt supported on non-porous titania catalyst (Pt/TiO2), while Pt supported on porous silica (Pt/SiO2) showed hysteresis [93,136,137].
Miller et al. reported hysteresis effect following pretreatment of Ru/RuO$_2$ catalyst that was attributed to arise from the changes in the catalyst structure [138]. Similar behavior was reported for CO oxidation on partially oxidized Pd nanoparticles, where slow hysteresis effects were found to depend on the pretreatment of catalyst samples [139]. Slavinskaya et al. [105] investigated the effect of structural and chemical states of palladium Pd/Al$_2$O$_3$ catalysts. They found that the destruction of large PdO particles and formation of smaller metallic palladium clusters resulted in the formation of core–shell structures, where the core was a PdO particle, and a shell formed by small PdO clusters, leading to self-sustained oscillations at different CO concentrations. The widening of hysteresis loop upon catalyst aging was attributed to morphological changes due to sintering of Pt particles, leading to different reduction and oxidation rates [55,94,140]. Casapu et al. investigated the effect of preparation method and the resulting morphological and structural properties of Pt nanoparticles, aging, temperature ramp rates, gas flows and CO concentrations on the hysteresis profile of CO oxidation for a Pt/Al$_2$O$_3$ catalyst (Figure 7) [94].
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Thermal inertia has been attributed to be responsible for surface and platinum oxide formation during extinction, to a CO-covered surface including Pt [82,84]. Carlsson et al. reported that the hysteresis associated with the slow transition from an oxygen-enriched leading preparation to a depend inhibiting species to small nanocrystalline and large structures, where oxidized Pt/Al2O3-pretreatment resulted in a considerable increase in hysteresis of CO oxidation, due to poisoning of the Pt active sites [55,94,140].

Heating and cooling rates and flow rates have been reported to affect hysteresis profiles [82]. Carlsson et al. reported that the hysteresis associated with the slow transition from an oxygen-enriched surface and platinum oxide formation during extinction, to a CO-covered surface including Pt reduction [55]. The different shape of hysteresis curves is attributed to inhibit accumulation of species on the surface during temperature ramp-up. Thermal inertia has been attributed to be responsible for

Figure 6. Temperature-programmed oxidation of 0.1 and 1% CO with 9% O2 over homogeneous (top panel) and heterogeneous (bottom panel) Pt/CeO2 monolith catalysts using heating/cooling rates of 5 °C/min [5].

Figure 7. CO oxidation light-off (solid lines, indicated by the arrows) and light-out (dotted lines) over the Pt/Al2O3 catalyst before and after hydrothermal aging [94].

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hysteresis effects in small-scale monolithic reactors [141]. Reduced activity during ignition process has been attributed to arise from CO poisoning and blocking of active sites at low temperatures. Hysteresis behavior is sensitive to local gas atmosphere, switching between normal and inverse hysteresis modes in complex gas mixtures. As a result, increased CO concentrations lead to a shift of the ignition toward higher temperatures due to the CO self-inhibition [5,54].

Differently-shaped hysteresis curves such as, normal, inverse or rectangular shape, occur due to inhibiting species accumulation on the surface during temperature ramp-up which was reported for nanocrystalline CuCr$_2$O$_4$ spinel catalysts in small-scale monolithic reactors, as shown in Figure 8. The small hysteresis is attributed to arise from high gas hourly space velocity (GHSV) of feed gas (60,000 mL/gh) which inhibits the formation of hot spots in the catalyst bed [142].

![Hysteresis effect during CO oxidation on CuCr$_2$O$_4$ spinel catalyst. Very small hysteresis (almost none) observed [142].](image)

**Figure 8.** Hysteresis effect during CO oxidation on CuCr$_2$O$_4$ spinel catalyst. Very small hysteresis (almost none) observed [142].

Koutoufaris et al. used a model of the reactor behavior under transient conditions to investigate the effect of self-inhibition on the reaction propagation along the catalyst and its impact on hysteresis. Results revealed essential mechanisms related to the formation and role of surface intermediates or inhibitors on the hysteresis behavior during CO oxidation with an increase in the hysteresis width as a result of self-inhibition, as shown in Figure 9a [141].
Figure 8. Hysteresis effect during CO oxidation on CuCr$_2$O$_4$ spinel catalyst. Very small hysteresis (almost none) observed [142].

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Figure 9. (a) Simulation results using different reaction and inhibition parameters. (b) Hysteresis magnitude as a function of self-inhibition parameter [141].

Mobini et al. reported inhibition effects on CuCr$_2$O$_4$ spinel catalyst [142]. It was reported that high feed gas concentration influenced increase or decrease in temperature for CO conversion, again arising due to inhibition of the formation of hot spots in the catalyst bed, as shown in Figure 9b, thus leading to a momentary transition from a high conversion to low conversion of CO oxidation reaction over this catalyst [142].

4. Analysis of Reviewed Literature

Hysteresis behavior is crucial for self-sustained low-temperature oxidation processes. Heterogeneous catalysts that exhibit hysteresis behavior over an extended temperature range are of primary importance. Several factors, such as particle size, gas pressure and the composition of gases, amongst others, decide the nature of catalyst suitable for use and the appropriate reaction conditions. Impurities on catalyst surfaces also affect the hysteresis behavior, as reported in the literature. Several studies report hysteresis for CO oxidation over a wide range of catalysts as summarized in Tables 1 and 2.
Table 1. Summary of the critical experiments which exhibited hysteresis.

| Gas Used       | Catalyst                                      | Hysteresis Type | Reference                  |
|----------------|-----------------------------------------------|-----------------|----------------------------|
| CO             | Pt/Al₂O₃                                      | Normal          | [5,30,85,94,114]           |
|                | Pt/TiO₂, Pt/SiO₂                              | Normal          | [93,136,137]               |
| CO and CH₄     | Pt/Al₂O₃ and Pt/CeO₂                          | Inverse         | [5,77,81]                  |
| CO             | PdO/Al₂O₃, Pd/Al(OH)₃, Pd/Mg(OH)₂             | Normal          | [105,135]                  |
| CO             | Cu-Ce/ZSM-5 or CuCe₁₋ₓZrₓO₇/ZSM-5             | Normal          | [72,92]                    |
| CO             | Unsupported Platinum wire, Platinum foil      | Normal          | [63,75]                    |
| CO, NO and C₃H₆| Unsupported Platinum                           | Inverse         | [5,49,67,91,111]           |
| CO             | Platinum and Palladium on alumina            | Normal          | [67,77,81–83]              |
| CO             | CuO                                           | Normal          | [63,117]                   |
| CO             | Gold nanoparticles                            | Normal          | [122–124]                  |
| CO             | Ceia-supported catalyst with 0.28 wt% gold (Au), Germanium (Ge) and Gadolinium (Gd) dopants | Normal          | [97,120,125]               |
| CO             | Pd/Ag, PdCu(110) alloys                      | Inverse         | [95,96]                    |
| CO             | Ru/RuO₂                                       | Normal          | [138]                      |

Table 2. Summary of the critical parameters and their effect on the exhibited hysteresis.

| Parameter                  | Effect on Hysteresis Curve                                                                 | Reference                                                                 |
|----------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Inlet CO concentration     | Increasing CO concentration in inlet gas causes a higher light-off temperature or ignition point, the hysteresis loop increases upon increasing the CO concentrations | [52,56,74,77,87,126,142]                                                   |
| Inlet Temperature          | Ignition and extinction shifted to higher temperatures with rapid increase in CO conversion | [77,128–134]                                                             |
| Surface Contamination and Aging | Increase in the hysteresis width due to the removal of contamination that blocks active sites | [75,94,141]                                                                 |
| Rate of temperature ramp-up | Increase in the temperature ramp-up result in shifting the ignition curve to higher temperatures | [72,92]                                                                   |
| Inhibition parameters      | Different inhibiting species accumulation on catalyst surface can change the shape of hysteresis curves and increase the width of the hysteresis. | [141,142].                                                                |
| Particle size              | When the size decrease (less than 2 nm), the hysteresis changes from normal to inverse. | [68,94,124]                                                               |

5. Conclusions

Hysteresis phenomena during CO oxidation has been studied intensively. However, explanations about its origin are conflicting as presented in the literature. Most of the experiments reported in the literature are scattered, and the range of catalysts and reactions used to study the hysteresis effect is minimal. Limited reports on hysteresis during CO oxidation relate this phenomenon to the structure and nature of the catalysts. Additionally, most of the data report the study of the CO conversion (%) as a function of the reactor inlet temperature instead of the reaction temperature, despite several studies discussing about creation of hotspots and the effect of reaction conditions and pretreatment conditions of catalysts. In order to improve the CO oxidation processes, a proper understanding of the conversion of CO is necessary.

The observed hysteresis phenomenon remains complex, and the reported literature is limited to specific catalysts or reaction parameters. New approaches are required to design and perform meaningful experiments. A systematic study of the hysteresis phenomenon on different catalysts should be conducted to answer many questions related to the effects of the wide range of reaction parameters, such as metal loading, pretreatment conditions, supports, aging, flow rate and heating rates. Based on the current trends surveyed in this review, the future probably has scope for further
progress and multidisciplinary efforts to come up with accurate explanations of this phenomenon that will certainly lead to other applications.

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