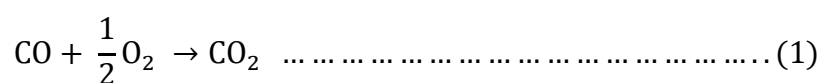


PREFACE

Carbon monoxide (CO) is one of the most poisonous gases and it is also known as a silent killer. It is colorless, odorless, tasteless and non-irritating gas, which makes it very difficult for human being to detect by physical sense. CO is emitted into the environment by incomplete combustion of carbon-containing fuels. There are several natural and anthropogenic sources of CO emission. Three main primary anthropogenic sources of CO emissions are residential, industrial and transportation. CO combines with haemoglobin present in blood cells of human-being and form carboxyhemoglobin, which reduces oxygen carrying capacity of the blood. CO has about 210 times greater affinity for haemoglobin than oxygen. Inhaling of CO can cause headache, fatigue, seizure, nausea, vomiting and at higher levels of exposure, disorientation, unconsciousness and even death. Poisonous nature of CO has stimulated intensive interest in the field of especially heterogeneous catalysis, investigations in the area of contact agents, which can operate effectively at ambient temperature. The catalytic oxidation of poisonous CO to non-poisonous carbon dioxide CO₂ is an important reaction (equation 1 below) in heterogeneous catalysis.



At low temperature conditions, CO oxidation is an important reaction in the applications like cold start exhaust emission control for automobiles, personal respiratory protective devices, proton exchange membrane fuel cells, chemical sensors, closed-cycle CO₂ lasers used for weather monitoring and air purification devices, etc. These include specialized heating, ventilation, air conditioning, rescue equipments, CO leak detection sensors, automotive emission control, ice arenas, indoor and underground

parking garages, smoking etc. It also has applications in regenerative CO₂ lasers used in orbiting applications for recombining dissociated CO₂ for weather monitoring and other remote sensing applications. Further, low temperature CO oxidation is vital in minimizing emissions during the cold start of an internal combustion engine. Preferential oxidation of CO in H₂ rich stream at low temperature is also significant for the effective operation of fuel cells in production of electricity. It has tremendous application assessment to the personal protective equipment (PPE) in respiratory protection systems for military, mining and fire fighting. It is also very useful in confined space protection such as submarines, deep sea welding and refuge chambers. Overall CO oxidation is vital in protecting vegetation and environment.

A variety of catalysts have been reported for oxidation of CO. The noble metals (Pt, Pd, Rh, Ru, Au), base metals (Cu, Mn, Cr, Co, Ni, Fe) and metal oxide (Cu₂O, ZnO, TiO₂, ZnO, CeO₂, ZrO₂) are widely used as catalysts for catalytic oxidation. The noble metal catalysts have high activity as well as thermal stability. Due to high cost, low availability, chemically sensitivity and stability in presence of fuel impurities, it is considered to be applied as an alternative base metal catalyst. Base-metal oxide catalysts including MnO, Fe₂O₃, Co₃O₄, NiO and CuO are relatively more active for low-temperature CO oxidation.

Towards the end of World War I, Lamb et al. (1920) discovered four-component (mixed oxides of Cu, Mn, Ag and Co) catalysts for use in gas mask canisters. Later, he focused on developing catalysts for use in coal mining and fire fighting situations and successfully obtained various catalysts. Many other researchers have also worked for catalytic control of CO in different conditions. Such catalysts are mainly of two types, either mono-metallic or bimetallic. Both forms are observed to be highly active at the room temperature, converting CO to CO₂ readily with high specific activity.

Copper manganese mixed oxides in the form of Hopcalite has been used as a catalyst for oxidation of CO at ambient temperature and it can be effective in respiratory protection, particularly in mining industries. The name hopcalite has been derived from the Johns Hopkins University ('Hop') and the University of California ('Cal'), in which this process fundamental investigation on CO oxidation was developed. Compared to other metal oxide catalysts, the hopcalite catalysts have many practical advantages due to their cost effectiveness, higher-availability and greater catalytic activity that result from their ability to provide active oxygen species by changing oxidation states. These types of catalysts are prepared by co-precipitation method and variables involved in the preparation procedure are known to control the catalytic activity.

The Ph.D. thesis having the title, '**Control of Carbon Monoxide Emission at Low Temperature Using Hopcalite Catalysts**', comprises of eleven chapters. Brief description about each is being presented below.

Chapter I: Introduction

Chapter 1 is introductory in nature, which explains various important sources of carbon monoxide, one of the most abundant air pollutants in the atmosphere. A brief discussion on Hopcalite (CuMnO_x) catalysts like various methods of preparations parameters and subsequent application for CO oxidation under different conditions is included. Important materials used as catalyst support and promoter are described in nutshell. Kinetics and mechanism of electron transfer over CuMnO_x catalysts for CO oxidation is also briefly discussed. Deactivation of Hopcalite catalysts by varied processes are also mentioned in this chapter.

Chapter II: Literature Review

Chapter II describes different conventional Hopcalite catalysts for CO oxidation in brief. Relevant literature survey is presented at a glance in tabular form. Literature review has helped to identify more suitable and effective Hopcalite catalysts for CO oxidation. Objectives of the present work are also included in this chapter and these are being enumerated here also as given below.

Chapter III: Experimental

This chapter presents various methodologies adopted for catalysts preparation, activity measurement and subsequent characterization studies. Characterization of the catalytic materials was carried out by a number of techniques such as Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Brunauer Emmett Teller (BET) estimation of the surface area. Principle of gas chromatography and its application for measuring CO conversion is also discussed in this chapter.

Chapter IV: Choice of precursor for synthesis of CuMnOx catalysts

Chapter IV describes the studies approach used for choice of precursors and subsequent calcination strategies on catalytic activity of various Hopcalite catalysts prepared for CO oxidation. Various precursors used for preparation of the Hopcalite catalysts have great influence on the activity of resulting catalysts for CO oxidation. The CuMnOx catalysts have been synthesized using $\{\text{Mn}(\text{Ac})_2 + \text{Cu}(\text{NO}_3)_2\}$, $\{\text{Mn}(\text{Ac})_2 + \text{Cu}(\text{Ac})_2\}$, $\{\text{Mn}(\text{NO}_3)_2 + \text{Cu}(\text{NO}_3)_2\}$, $\{\text{Mn}(\text{NO}_3)_2 + \text{Cu}(\text{AC})_2\}$ as precursor precipitated by KMnO_4 solution and their activity for CO oxidation has been evaluated. The catalyst prepared by $\{\text{Mn}(\text{Ac})_2 + \text{Cu}(\text{NO}_3)_2\}$ as a precursors exhibited the best catalytic activity

towards CO oxidation due to their high oxygen mobility. Effectiveness of CuMnOx catalysts has prompted a big deal of fundamental work devoted for clarifying the role of each component as well as the nature of active sites.

Chapter V: Choice of precipitant in precursor for synthesis of CuMnOx catalysts

Chapter V describes the studies conducted for measurement of activity of the prepared CuMnOx catalysts for CO oxidation. Activity was found to depend strongly on the precipitant used in the preparation of catalyst. The precipitate obtained by co-precipitation leads to phase changes towards thermodynamically more stable structures. The present work is an attempt to examine the effect of various precipitation agents such as KMnO₄, Na₂CO₃ or KOH on the physicochemical and catalytic properties of CuMnOx catalyst for CO oxidation. The catalyst prepared by KMnO₄ as a precipitant exhibited the best catalytic activity towards CO oxidation due to the high oxygen mobility. This preparation method showed a very significant influence on structural properties and catalytic activity of the Hopcalite catalysts for CO oxidation. Thus, the choice of precipitant was observed to be very important in designing the most efficient CO oxidation catalyst.

Chapter VI: Optimization of preparation conditions for catalytic activity of CuMnOx catalysts

Chapter VI discusses about various optimization parameters used in preparation of the Hopcalite catalyst for CO oxidation at a low temperature. The preparation parameters such as Cu:Mn molar ratios, drying temperature, calcination temperature and calcination time exerted strong influence on activity of the resultant catalysts. The Cu oxide was found to be poorly active for CO oxidation but, in combination with Mn oxide in appropriate proportions, certain very active catalyst systems are generated,

which are studied and optimized further. The preparation conditions of CuMnOx catalyst for getting excellent catalytic activity are 1/8 (Cu: Mn) molar ratio at 110°C drying temperature for 24h, followed by calcination at 300°C for 2h. The optimum operating parameters for CO oxidation is 100mg weight of catalyst at a flow rate of CO (1.5ml/min).

Chapter VII: Effect of promoter doping on catalytic activity of Cu₁Mn₈ for CO oxidation

Chapter VII describes about addition of (3%) cobalt, cerium, iron and silver promoters doping to a mixed Cu₁Mn₈ precursor to improve catalytic performance for CO oxidation. Addition of quite low concentrations of these promoters to the Cu₁Mn₈ catalysts proved very beneficial. The order of activity for different types of doped and un-doped Cu₁Mn₈ catalyst for CO oxidation is as follows: 3%AgCuMn₈Ox > 3%CeCuMn₈Ox > 3%FeCuMn₈Ox > 3%CoCuMn₈Ox > Cu₁Mn₈ catalyst. The Cu₁Mn₈ catalyst doped with (3wt.%) silver have a higher catalytic activity as compared to the other catalysts. Activities of different doped Cu₁Mn₈ catalysts were attempted to be understood in light of their characterization by various techniques like XRD, SEM-EDX, FTIR, XPS and BET.

Chapter VIII: Effect of (Ce, Ag and Au) doping on catalytic activity of Cu₁Mn₈ catalysts

Chapter VIII discusses about addition of different types of noble metals (Ag and Au) as dopants into the CeCuMn₈Ox catalyst for improving their performance in CO oxidation. New active surface sites created by the doping resulted in enhancement of the catalytic activity. Addition of relatively smaller amount (1.5wt.%) of CeOx into Cu₁Mn₈ catalyst improved the performance significantly for CO oxidation. Further,

addition of (1wt.%) AgO₂ or (0.5wt.%) AuOx to 1.5%CeCuMn₈Ox catalyst also enhanced their activity. The order of activity of the catalysts for CO oxidation is as follows: 1.5%Ce0.5%AuCuMn₈Ox > 1.5%Ce1.0%AgCuMn₈Ox > 1.5%CeCuMn₈Ox > Cu₁Mn₈.

Chapter IX: Optimization of 3%AgCuMn₈Ox loading on γ -Al₂O₃ support

Chapter IX describes about the effects of γ -Al₂O₃ support on performance of 3%AgCuMn₈Ox catalyst applied for CO oxidation. The activity of 3%AgCuMn₈Ox/Z% γ -Al₂O₃ catalyst could also be interpreted in light of the characterization results and it was confirmed that Cu⁺, Mn²⁺, Ag and Al existed mostly on the active surface sites of 3%AgCuMn₈Ox/Z% γ -Al₂O₃ catalysts. The optimum metals loading on γ -Al₂O₃ support is 40%. The γ -Al₂O₃ support was used in catalyst for improving the performance and also, for reducing the cost.

Chapter X: Chemical Kinetics of CO oxidation

Chapter X presents kinetic aspects of the reaction occurring in case of the best 3%AgCuMn₈Ox/60% γ -Al₂O₃ catalyst. The power law rate expression is developed for the reaction. The values of the pre-exponential factor and activation energy have been calculated using the experimental data obtained in the temperature range of 25-30°C. The rate of CO oxidation by the power law expression as given below (equation 2)

$$\text{Rate } (-r_p) = 7.165 \times 10^5 \exp(-50261/RT) (C_{CO})^{0.99} \text{ g.mol/gcat.h} \dots\dots\dots (2)$$

Value of the activation energy is found to be 50.26 kJ/mol, which was the least in comparison to the activation energy observed for different catalysts reported in the literature for CO oxidation. The order of the reaction for CO oxidation on this 3%AgCuMn₈Ox/60% γ -Al₂O₃ catalyst is found to be of the first-order.

Chapter XI: Conclusions

Chapter XI reports the conclusions based on the experimental work. Discussion and further scope of work in this area is also included in the Ph.D. thesis.