

Literature Review

2. General

The performance of catalysts are great functions of some parameters such as the degree of contact between CO and catalyst, feed composition, preparation method, (Cu:Mn) molar ratio and calcination temperature, etc [Paldey *et al.*, 2005]. Many hopcalite catalysts have been examined for their activity in CO oxidation. They are many synthesis methods have been developed to improve the performance of hopcalite catalyst, including impregnation, co-precipitation, sol-gel, supercritical anti-solvent precipitation and reduction process. The redox behavior of copper (Cu) and manganese (Mn) species is mainly affecting the reactivity in CO oxidation [Njagi *et al.*, 2010; Badr and Probert 1994]. It is accepted that the oxygen species associated with Cu in the CuMnOx catalyst are very active and may be dominated by the low-temperature catalytic oxidation. In characterization points to increase the reactivity of lattice oxygen associated with the Cu species as well as the mobility of lattice oxygen from Mn species [Shi *et al.*, 2015].

The promoters are very much use in the CuMnOx catalyst due to their remarkable influence on the reactivity and stability. The different promoters are added less than 10% into the CuMnOx catalyst to get better performance for CO oxidation. The Cu-oxide is found poorly active for CO oxidation, but in conjunction with Mn-oxide in appropriate proportions, some very active catalyst system was generated [Hasegawa *et al.*, 2009]. The catalytic oxidation of CO has performed in a series of quick steps, while the adsorption of CO proceeded quickly therefore limited desorption of CO₂. In most of the above cases, the oxidation of CO has been carried out at a low temperature [Chen *et al.*, 2009]. The light-off characteristic was representing the activity of the CuMnOx

catalysts with the increasing of temperature. The characteristic temperature T_{10} , T_{50} and T_{100} corresponds to the initiation of oxidation, 50% conversion and complete conversion of CO respectively. The rising temperature is enlarge the specific surface area and pore volume of the catalyst, it causes, activity of the catalyst has been increased.

Table 2.1: Application of various hopcalite catalysts for CO oxidation

Catalyst	Catalyst Preparation Method	Operating Parameters	Remarks	References
Hopcalite and their derivatives				
Prepared by Co-precipitation method				
CuMnOx	Co-precipitation method	100mg catalyst with a gas mixture consisting of (50% O ₂ , 48% N ₂ and 2% CO) and total flow rate of 23 ml/min.	CuMnOx $T_{10}=80^{\circ}\text{C}$, $T_{50}=170^{\circ}\text{C}$, $T_{100}=260^{\circ}\text{C}$	Puckhaber <i>et al.</i> , 1989
CuMn ₂ O ₄	Co-precipitation method	100mg catalyst with feed gas consisted of (5% CO in He, 5ml/min) and O ₂ (50 ml/min) at temperature 20°C and total GHSV was 33,000 h ⁻¹	CuMn ₂ O ₄ $T_{100}=20^{\circ}\text{C}$ for Time=12hr.	Hutching <i>et al.</i> , 1996
CuMn ₂ O ₄	Co-precipitation method	100mg catalyst; typically CO (5% CO in He, 5ml/min), O ₂ (50ml/min) and GHSV was 33000/h.	CuMn ₂ O ₄ $T_{50}=32^{\circ}\text{C}$, $T_{100}=80^{\circ}\text{C}$	Hutchings <i>et al.</i> , 1998
CuMn ₂ O ₄	Co-precipitation method	100mg catalyst, (0.45vol% CO), at flow rate (20ml/min) with CO (5% CO in He, 5ml/min) and O ₂ (50ml/min) and GHSV was 3300/h.	CuMn ₂ O ₄ $T_{70}=30^{\circ}\text{C}$ Const., Time = 30min	Taylor <i>et al.</i> , 1999
CuMn ₂ O ₄	Co-precipitation	200mg catalyst with a gas mixture consisting of (3% CO and 3% O ₂ in	CuMn ₂ O ₄ $T_{10}=90^{\circ}\text{C}$,	Fortunato <i>et al.</i> , 2000

	method	He) with a total flow rate of (30 ml/min), at temperature 52°C.	T ₅₀ =160°C, T ₁₀₀ = 220°C	
Cu/MnOx catalysts	Co-precipitation method	100mg catalyst with a gas mixture consisting of (37.5% H ₂ , 1.25% CO, 25.0% H ₂ O, 12.5% CO ₂ , and N ₂ balance) at a space velocity of 6400 h ⁻¹ .	Cu/MnOx catalysts T ₁₀ =200°C, T ₅₀ = 220°C, T ₁₀₀ =250°C	Tanaka <i>et al.</i> , 2003
CuMn ₂ O ₄	Co-precipitation method	100mg catalyst in the feed gas (0.25% CO, 5% O ₂ balance He) and total flow rate was 60 ml/min.	CuMn ₂ O ₄ X _{co} =80%, at temp. 30°C, Time= 10hr.	Mirzaei <i>et al.</i> , 2003
CuMnOx	Co-precipitation method	100mg catalyst, with a gas mixture consisting of (1% CO, 99% dry air) and total flow rate was 80 ml/min.	CuMnOx T ₈₀ =25°C for time 10 min.	Mirzaei <i>et al.</i> , 2013
Au/CuMnOx	Co-precipitation method	100mg catalyst, total flow rate 22.5 ml/min, molar ratio (CO: O ₂ : He = 1: 89: 10), reaction temperature 30°C and time on-line of 1000 min.	Au/CuMnOx T ₇₀ =30°C Constant, Time= 1000 min	Solsona <i>et al.</i> , 2004
Cu _{1.5} Mn _{1.5} O ₄	Co-precipitation method	100mg catalyst with total flow rate 1000ml/min; (CO: 4.0 vol.%; O ₂ : 20vol.%, balance He) and heating rate 12°C min ⁻¹ , (SV=310,000/h).	Cu _{1.5} Mn _{1.5} O ₄ T ₁₀ =75°C T ₅₀ = 110°C, T ₁₀₀ = 120°C	Paldey <i>et al.</i> , 2005
CuMnOx	Co-precipitation method	250mg catalyst with specific velocity was 45,000h ⁻¹ , time 50min and initial concentration of CO was 3 × 10 ⁻⁵ to 5 × 10 ⁻⁵ mol L ⁻¹ .	CuMnOx T ₁₀ =40°C, T ₅₀ =80°C, T ₆₅ =100°C Const.	Li <i>et al.</i> , 2007

Cobalt doped CuMnOx	Co- precipitation method	100mg catalyst with 5000 vppm CO in air and GHSV velocity was 33,000 h ⁻¹ .	Cobalt doped CuMnOx T ₁₀ =80°C, T ₅₀ =120°C, T ₆₅ =160°C Const.	Jones <i>et al.</i> , 2008
CuMnOx	Co- precipitation method	300mg catalyst with a gas mixture consisting of 3% CO in air with a total flow rate of 100 ml/min.	Cu ₁ Mn ₉ T ₁₀ =130°C, T ₅₀ = 170°C, T ₁₀₀ = 190°C Cu ₃ Mn ₇ T ₁₀ =110°C, T ₅₀ = 175°C, T ₁₀₀ = 200°C Cu ₈ Mn ₂ T ₁₀ =120°C, T ₅₀ = 160°C, T ₁₀₀ = 190°C	Morales <i>et al.</i> , 2006
CuMnOx	Co- precipitation method	100mg catalyst with 5000vppm CO in air and GHSV of 33,000h ⁻¹	CuMnOx T ₁₀ =16°C, T ₅₀ = 30°C Const. Time =90 min	Jones <i>et al.</i> , 2009
CuMnOx	Co- precipitation method	300mg catalyst in presence of (1.5vol.%CO, 2.5vol.% O ₂ balanced He) with a total flow rate of 80mL/min.	CuMnOx T ₁₀ =115°C, T ₅₀ = 180°C, T ₁₀₀ = 218°C	Chen <i>et al.</i> , 2009
CuMnOx	Redox method	100mg catalyst in presence of (1% CO, 2%O ₂ and 5%N ₂ in He), space velocity 35,000 mLh ⁻¹ gcat ⁻¹ .	CuMnOx T ₅₀ = 25°C, T ₁₀₀ =35°C	Njagi <i>et al.</i> , 2011

Au/CuMnOx	Deposition precipitation method	Au/CuMnOx catalysts aged for 0.5h at 25°C temperature, 5000vppm CO in air, GHSV = 12,000 h ⁻¹	Au/CuMnOx T ₁₀₀ =50°C, Time =20 min	Cole <i>et al.</i> , 2010
CuMnOx	Redox method	100mg catalyst in presence of (1%CO, 1%O ₂ , 60% H ₂ balanced N ₂) with a total flow rate of 50ml/min and space velocity 35,000mL/h.g _{cat} .	CuMnOx T ₁₀ =4°C,T ₅₀ = 12°C, T ₁₀₀ = 25°C	Njagi <i>et al.</i> , 2010
CuMn ₂ O ₄	Conventional precipitation method	50mg catalyst at 25°C temperature with space velocity 12000h ⁻¹ , presence in a premixed cylinder (5000ppm CO in air).	CuMn ₂ O ₄ T ₇₀ =25°C for 40 min.	Tang <i>et al.</i> , 2011
Nanosized Cu-Mn spinel	Co-precipitation method	130mg catalyst in presence of (1 Vol.% CO, 2Vol.% O ₂ , balanced N ₂) with a total flow rate of 100ml/min and space velocity was 30,000mL/hg _{cat} .	CuO/TiO ₂ T ₁₀ =190°C,T ₅₀ = 260°C, T ₁₀₀ = 360°C Mn ₃ O ₄ /TiO ₂ T ₁₀ =200°C,T ₅₀ = 220°C, T ₁₀₀ = 340°C Cu _{1.5} Mn _{1.5} O ₄ T ₁₀ =150°C,T ₅₀ = 210°C, T ₁₀₀ = 280°C	Behar <i>et al.</i> , 2012
CuMnOx	Co-precipitation method	200mg catalyst with space velocity: 20,000mLh ⁻¹ g _{cat} ⁻¹ and feed gas consisted of (1% CO, 20% O ₂ and 79% N ₂).	CuMnOx T ₁₀ =12°C T ₅₀ = 30°C,T ₁₀₀ =50°C	Cai <i>et al.</i> , 2012

$\text{Cu}_{1.2}\text{Mn}_{1.8}\text{O}_4$	Co-precipitation method	100mg catalyst in presence of (5% CO in He), O_2 (50ml/min), total GHSV of $33,000 \text{ h}^{-1}$ and a 0.45 mol% of CO concentration.	$\text{Cu}_{1.2}\text{Mn}_{1.8}\text{O}_4$ $T_{100}=170^\circ\text{C}$	Mirzaei <i>et al.</i> , 2003
CuMnOx	Co-precipitation method	100mg catalyst at temperature 25°C with 5000ppm CO in air.	CuMn_2O_4 $X_{\text{Co}}=40\%$ at temp. 25°C for 20 min.	Clarke <i>et al.</i> , 2015
CuMnOx	Co-precipitation method	200mg catalyst with feed gas (1% CO, 20% O_2 and 79% N_2) and a space velocity $20,000 \text{ mLg}^{-1}\text{h}^{-1}$.	CuMnOx $T_{10}=13^\circ\text{C}$, $T_{50}=30^\circ\text{C}$, $T_{100}=70^\circ\text{C}$	Shi <i>et al.</i> , 2015
Cu supported CeMnO_2	Co-precipitation method	210mg catalyst in the feed gas composition (2% CO, 2% O_2 and 96% H_2) with space velocity 20000 h^{-1} .	Cu/CeO_2 $T_{10}=55^\circ\text{C}$, $T_{50}=80^\circ\text{C}$, $T_{100}=130^\circ\text{C}$ $\text{Cu/Ce}_{0.9}\text{Mn}_{0.1}\text{O}_2$ $T_{10}=30^\circ\text{C}$, $T_{50}=65^\circ\text{C}$, $T_{100}=120^\circ\text{C}$	Hoshyar <i>et al.</i> , 2015
CuMnOx addition SnO_2	Co-precipitation method	100mg catalyst in the feed gas composition of (1% CO, 21% O_2 balanced N_2), total flow rate 30mL/min and corresponding space velocity was $18,000 \text{ mL/h/g}_{\text{cat}}$.	CuMnOx $T_{10}=30^\circ\text{C}$, $T_{50}=56^\circ\text{C}$, $T_{100}=85^\circ\text{C}$ CuMnOx-10.6 wt.% SnO_2 $T_{10}=20^\circ\text{C}$, $T_{50}=30^\circ\text{C}$, $T_{100}=40^\circ\text{C}$	Gardner and Hoflund 1991

$\text{Co}_x\text{Mn}_{3-x}\text{O}_4$	Precipitation method	50mg catalyst in presence of (0.8% CO, 20%O ₂ in Ar) and heating rate 2°C/min with a total flow rate of 1.63 ml/Sec.	$\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ $T_{10}=25^\circ\text{C}, T_{50}=50^\circ\text{C}, T_{100}=80^\circ\text{C}$	Behar <i>et al.</i> , 2012
Cu/Ni/Co/Fe doped MnO ₂ nano-wires	Deposition–precipitation method	50mg catalyst in presence of 1% CO and 20%O ₂ balanced with N ₂ at a mass flow rate 30mL/min corresponding to a GHSV was 36,000mL/g/h.	MnO_2 $T_{10}=150^\circ\text{C}, T_{50}=225^\circ\text{C}, T_{100}=275^\circ\text{C}$ $\text{Cu}_{0.1}\text{MnO}_x$ $T_{10}=35^\circ\text{C}, T_{50}=75^\circ\text{C}, T_{100}=100^\circ\text{C}$ $\text{CuO}_{0.1}/\text{MnO}_2$ $T_{10}=65^\circ\text{C}, T_{50}=120^\circ\text{C}, T_{100}=160^\circ\text{C}$ $\text{Co}_{0.1}\text{MnO}_x$ $T_{10}=100^\circ\text{C}, T_{50}=125^\circ\text{C}, T_{100}=165^\circ\text{C}$ $\text{Ni}_{0.1}\text{MnO}_x$ $T_{10}=120^\circ\text{C}, T_{50}=175^\circ\text{C}, T_{100}=220^\circ\text{C}$ $\text{Fe}_{0.1}\text{MnO}_x$ $T_{10}=150^\circ\text{C}, T_{50}=215^\circ\text{C}, T_{100}=250^\circ\text{C}$	Gao <i>et al.</i> , 2016

Cu-Mn/Al ₂ O ₃ Cu-Ni/Al ₂ O ₃	Co-precipitation method	100mg catalyst in presence of 1vol% CO, 1vol%O ₂ , 60vol% H ₂ and He balance. The GHSV was vary within 30,000-90,0000/h.	Cu-Mn/Al ₂ O ₃ T ₁₀ =60°C, T ₅₀ = 120°C, T ₁₀₀ = 200°C Cu-Ni/Al ₂ O ₃ T ₁₀ =60°C, T ₅₀ = 120°C, T ₁₀₀ = 200°C	Dasireddy <i>et al.</i> , 2018
La/CuMnOx	Co-precipitation method	500mg catalyst in presence of 14.6% CO, 23.8% CO ₂ , 39.7% H ₂ and the balance gas was Ar and the space velocity was maintained at 6400 NmL/g.h	La/CuMnOx T ₁₀ =140°C, T ₅₀ = 225°C, T ₁₀₀ = 300°C	Runxia <i>et al.</i> , 2016
CuMnOx/ SnO ₂	Co-precipitation method	100mg catalyst in presence of 1% CO, 21% O ₂ and balanced N ₂ , with a flow rate of 30mL/min, which corresponds to a space velocity of 18,000mL/h.gcat).	CuMnOx T ₁₀ =30°C, T ₅₀ = 55°C, T ₁₀₀ = 85°C CuMnOx- SnO ₂ T ₁₀ =20°C, T ₅₀ = 30°C, T ₁₀₀ = 50°C	Liu <i>et al.</i> , 2016
CuMnOx	Co-precipitation method	50mg catalysts in presence of 1vol.% CO and 10vol.% O ₂ balanced N ₂ with a total flow rate of 20mL/min and space velocity of 24,000mL g ⁻¹ h ⁻¹ .	CuO T ₁₀ =90°C, T ₅₀ = 130°C, T ₁₀₀ = 170°C MnOx T ₁₀ =55°C, T ₅₀ = 75°C, T ₁₀₀ = 110°C	Li <i>et al.</i> , 2017

			CuMnOx T ₁₀ =20°C, T ₅₀ = 30°C, T ₁₀₀ = 45°C	
Prepared by Sol-gel method				
CuMnOx	Sol-gel method	100mg catalyst with flow rate of 30,000ml/gh at reaction temperature 60-120°C at a total flow rate of 50 ml/min.	CuMnOx T ₁₀ =60°C, T ₃₀ =120°C Const.	Kramer <i>et al.</i> , 2006
CuMnOx	Sol-gel method	The (Cu/Mn = 1/2), W/F: 1.0*10 ⁻³ min.g-cat.mL ⁻¹ at a flow rate: 50mL/min with a gas composition (1vol% CO, 1vol% O ₂ , 60vol% H ₂ and balance N ₂).	CuMnOx T ₁₀ =30°C T ₅₀ = 80°C, T ₁₀₀ = 120°C	Hasegawa <i>et al.</i> , 2009
Prepared by Impregnation method				
CuMn ₂ O ₄	Impregnation method	50-400mg catalyst in presence of (17%CO in air) employed as a reactant feed with total flow rate of 180ml/min.	CuMn ₂ O ₄ T ₁₀ =200°C, T ₅₀ = 240°C, T ₁₀₀ =320°C	Severino <i>et al.</i> , 1998
CuOx additives Mn ₂ O ₃ , Cr ₂ O ₃ , WO ₃	Impregnation method	100mg catalyst with a gas mixture consisting of (1% CO, 1% O ₂ , 50% H ₂ and balanced N ₂) at a total flow rate of 60 ml/min with GHSV was 30,000 h ⁻¹ .	CuOx-Mn ₂ O ₃ T ₁₀ =50°C, T ₅₀ = 160°C T ₁₀₀ = 220°C CuOx-Cr ₂ O ₃ T ₁₀ =60°C, T ₅₀ = 190°C, T ₁₀₀ = 225°C CuOx-WO ₃ T ₁₀ =100°C,	Zaki <i>et al.</i> , 2009

			$T_{50}=335^{\circ}\text{C}$, $T_{80}=400^{\circ}\text{C}$ Const.	
Cu–Co and Cu-Mn oxides	Impregnation method	100mg catalyst with a gas mixture: consisted of 2% CO in air and total flow rate maintained at 50 ml/min.	Cu–Co $T_{10}=60^{\circ}\text{C}$, $T_{50}=300^{\circ}\text{C}$ Const. Cu-Mn $T_{10}=60^{\circ}\text{C}$, $T_{50}=550^{\circ}\text{C}$ Const.	Wojciechowska <i>et al.</i> , 2007
CuMnOx KOH-CuMnOx	Impregnation method	8–40g catalyst with gas mixture consisting of (0.4% CO, 1.0% CO ₂ and air) with a total flow rate of 500mL/min and temp. increased with a rate of 20°C/min.	CuMnOx $T_{10}=60^{\circ}\text{C}$, $T_{50}=110^{\circ}\text{C}$, $T_{100}=160^{\circ}\text{C}$ KOH-CuMnOx $T_{10}=50^{\circ}\text{C}$, $T_{50}=80^{\circ}\text{C}$, $T_{100}=120^{\circ}\text{C}$	Guo <i>et al.</i> , 2016
Prepared by Incipient wetness impregnation method				
Ce/CuMn ₂ O ₄	Incipient wetness impregnation method	250mg catalyst in presence of 1% CO, 1.25% O ₂ and 50% H ₂ (He balance), at a flow rate of 1000cm ³ min ⁻¹ g ⁻¹ (GHSV = 80,000h ⁻¹) and using a heating ramp of 5°Cmin ⁻¹ .	CuMn ₂ O ₄ $T_{10}=40^{\circ}\text{C}$, $T_{50}=200^{\circ}\text{C}$, $T_{70}=250^{\circ}\text{C}$ Const. Ce/CuMn ₂ O ₄ $T_{10}=40^{\circ}\text{C}$, $T_{50}=115^{\circ}\text{C}$, $T_{100}=165^{\circ}\text{C}$	Elmhamdi <i>et al.</i> , 2017
CuO/MnO ₂	Incipient wetness impregnation method	50mg catalyst in presence of (1%CO, 99% dry air) with a feed rate 20ml/min, and space velocity was 24,000mL/g _{cat} /h.	CuO $T_{10}=140^{\circ}\text{C}$ $T_{50}=200^{\circ}\text{C}$, $T_{100}=415^{\circ}\text{C}$	Qian <i>et al.</i> , 2013

			<p>MnO₂</p> <p>T₁₀=60°C, T₅₀= 100°C, T₁₀₀= 160°C</p> <p>CuO/MnO₂</p> <p>T₁₀=30°C, T₅₀= 60°C, T₁₀₀= 100°C</p>	
Prepared by Reactive Grinding method				
CuMnOx	Grinding and precipitation method	50mg catalyst in presence of (5000ppm CO in air) at a flow rate of 22.5 ml/min.	<p>CuMnOx</p> <p>T₁₀=120°C, T₅₀= 190°C, T₁₀₀=240°C</p>	Kondrat <i>et al.</i> , 2011
CuMn ₂ O ₄	Grinding ball mill method	50mg catalyst at a flow rate of 21 ml/min and GHSV was 12000h ⁻¹ at temp. 25°C with 5000ppm CO in air.	<p>CuMn₂O₄</p> <p>X_{CO}=40% at temp. 25°C, Time= 72 hr.</p>	Clarke <i>et al.</i> , 2015
Prepared by Flame spray pyrolysis method				
Cu _{1.5} Mn _{1.5} O ₄ nanoparticle	Precipitation method and Flame sprays pyrolysis	100mg catalyst (0.67vol.% CO, 66vol.% N ₂ and 33.33vol.% O ₂) at temp. 300°C for 20 min and total flow rate of 100ml/min.	<p>Cu_{1.5}Mn_{1.5}O₄ nanoparticle</p> <p>T₁₀=25°C, T₅₀= 50°C, T₁₀₀= 110°C</p>	Biemelt <i>et al.</i> , 2015
CuO/CeMnO	Urea nitrate combustion method	500mg catalyst in presence of 1vol.% CO in air with GHSV was 52000mL/(g.h).	<p>Ce-Mn-O</p> <p>T₁₀=225°C, T₅₀= 270°C, T₇₀= 350°C Const.</p>	Fuzhen <i>et al.</i> 2015

			CuO/Ce-Mn-O $T_{10}=100^{\circ}\text{C}, T_{50}=$ $120^{\circ}\text{C}, T_{100}=$ 160°C	
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The activity of hopcalite catalyst is strongly depending upon the nature of metal ions concentration and their allocation in the crystal lattice. The Mn-based catalysts are very active for CO oxidation and it needed tetravalent Mn but, Mn (IV) compounds are usually unstable at the high temperature; therefore, the addition of Cu compounds increased their stability and activity also [Behar *et al.*, 2012; Qian *et al.*, 2013]. The presence of MnO₂ in a highly amorphous form is an assertion for a high surface area for contacting with the Cu atoms, which was a prerequisite for the high activity of a hopcalite catalyst. In the spinel CuMn₂O₄ catalyst containing more than one transition metal ion per unit, the distribution and valence sites of the cations among both the tetrahedral (A sites) and octahedral (B sites) sub-lattices of the spinel structures [Mirzaei *et al.*, 2003]. The electronic configuration of Cu(I) occupies in the CuMn₂O₄ spinel structure, the octahedral sites, where they are subjected to larger extra-atomic relaxation energy. In the CuMnOx catalyst presence of manganese oxide ability to absorb activate oxygen and subsequent, the inclusion of copper to improve and stabilize active phases. The structural defects connected with the oxygen vacancies and the Mn₂O₃ high distribution on the catalytic surface facilitates the catalyst reducibility [Morales *et al.*, 2006; Clarke *et al.*, 2015].

The cobalt doped CuMnOx (CuCoMnO₄) catalyst has a highest specific activity towards CO oxidation as well as the highest specific surface area. The doping of Zn into the CuMnOx catalyst is widely used as a hydrogenation or dehydrogenation reaction. The interface of Cu with ZnOx and the oxidation state of Cu are supposed to be concerned

as the active sites during the catalytic processes. The synergy effects are arises, the contact of Cu with ZnO being the binary catalyst, which was more dynamic than the each component [Jones *et al.*, 2008; Cai *et al.*, 2012]. From the TEM and XRD analysis revealed that the CuMnOx catalyst mixed with Fe₂O₃ and Mn₃O₄ the particle size changes, therefore the activity of catalyst has been increased [Biemelt *et al.*, 2015]. Ceria has a high oxygen storage ability and well known catalytic and redox properties (Ce⁴⁺/Ce³⁺), it's making more oxygen availability for the CO oxidation process. Presence of Ce into the CuMnOx catalyst exhibited that the excellent water resistance for CO oxidation. The CeO₂ enriched surface of CuMnOx catalyst, preferential for CO oxidation [Hoshyar *et al.*, 2015]. The different oxide support over the CuMnOx catalyst improved their overall activity and the mixed oxides are characterized by high electron mobility and positive oxidation states. The binary CuMnOx loaded transition metal oxides have an outstanding potential for practical applications to reduce CO in the environment [Guo *et al.*, 2016].

An addition of Au or Ag into the CuMnOx catalyst, it will raise the number of active sites present on the catalyst surface; therefore, the activity of the CuMnOx catalyst for CO oxidation has been increased [Solsona *et al.*, 2004]. The metal oxides and supported noble metal oxides are active for many deep oxidation reactions. The mechanism of catalytic oxidation involves both the lattice and surface oxygen for reducing metal sites on supported noble metals. The adsorbed CO has been observed during the oxidation on Pt/CuMnOx therefore; it can be concluded that CO adsorbed on oxidized Pt is not taking part in the reaction [Cole *et al.*, 2010]. The noble metals like Pt, Pd and Au, are said to function in the reduced state at all the conditions. The mechanism of CO oxidation over the noble metal catalyst may be different from the other metal oxide catalysts. The noble metal catalysts may be following either a Langmuir-Hinshelwood

type of mechanism (reaction between an adsorbed reactant and adsorbed oxygen) or an Eley-Rideal mechanism (reaction between adsorbed oxygen and a gas-phase reactant molecule). On Ag, the oxygen chemisorptions are fairly very strong, with a transfer of electrons to the oxygen taking place and on Pd, however, oxygen adsorption is relatively weak [Santra and Goodman 2002].

An additional of Pt or Pd in CuMnOx catalyst has shows that oxidation occurs faster in the air than pure oxygen due to the creation of a relatively stable Pt species in highly oxidizing environments. It is found that Pd/CuMn₂O₄ catalyst is more active for CO oxidation as compared to Pt/CuMn₂O₄ or Au/CuMn₂O₄ catalyst, without any noticeable deactivation [Spivey 1987]. The palladium oxide (PdO_x) primarily exists in a distinct oxidation state. It was only reduced to Pd metal and will decompose on extensive contact with the atmosphere. The ionization energies of PdO_x are successfully applied in a hopcalite catalyst. The noble metal makes a strong bond with the CuMnOx catalyst, and they are active enough to bond with the gaseous molecules without irreversible poisoning [Zhou *et al.*, 2014]. Pt is more actively promoter than Pd or Rh. The best part of CO oxidation over the (Pt:Pd) catalysts has been conducted under the lean O₂ conditions. This is appropriate to the automotive exhaust catalyst. The monometallic Pt and Pd displayed higher activity than the bimetallic catalysts. The precious metals are highly able for reducing under atmospheric conditions to some extent [Yao 1983].

In this chapter, many issues relating to the oxidation of CO over metal oxide catalysts, which have arisen in literature over the past century, are discussed. Special interest has been given to the probable applications of these catalysts, preparation of active species and promotion of catalysis in these systems. The limitations of using metal oxide based catalytic systems are also recognized and explored with the aim of introducing and giving an understanding of the experimental results contained in later chapters. Carbon

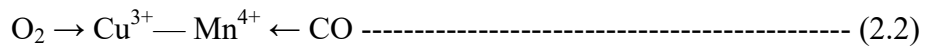
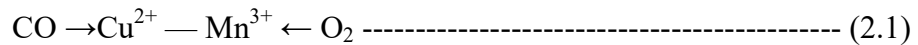
monoxide is a pollutant of industrial and domestic origin with a well publicized history of serious health implications. Emission control using catalytic oxidation has many advantages over adsorption methods in terms of size of equipment, cost and operating simplicity [Badr and Probert 1994]. Further discrepancies arise in the literature when considering the valences of the copper and manganese ions in hopcalite. A series of magnetic and structural investigations of CuMn_2O_4 lead to a number of researchers suggesting Cu and Mn to be the most stable configuration of the mixed oxide. Others recommended that Cu^+ in the presence of Mn^{4+} was the most viable environment. Both configurations have been supported by electronic measurements. In these Cu–Mn catalyst systems, the catalytic activity was strongly affected by the transition of the catalyst from an amorphous to a crystalline phase [Behar *et al.*, 2012; Biemelt *et al.*, 2015]. Metal oxides and mixed metal oxide systems with spinel-like structure have received significant consideration because of their great electrical and magnetic properties. It has been reported that these properties are influenced by the nature of the metal ions and their allocation in the crystal lattice [Choi *et al.*, 2016; Clarke *et al.*, 2015].

2.1 Structure of copper manganese oxides

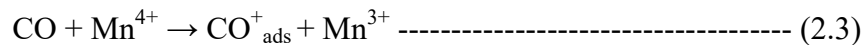
A structural investigation of CuMn_2O_4 by X-ray diffraction was carried out by Jones and co-workers. A prior was thought that CuMn_2O_4 , in analogy with CuFe_2O_4 , CuCr_2O_4 and other cupric compounds, should have a tetragonal pseudo-spinel structure with inverse arrangement of cations [Jones *et al.*, 2009]. It was expected Cu^{2+} had displaced Mn^{3+} from the octahedral sites in the spinel and both the Cu^{2+} and Mn^{3+} have substantial Jahn-Teller stabilization energies, significant distortion from the cubic symmetry would be expected [Kireev *et al.*, 2009]. The nature of active sites present in the CuMn_2O_4 catalyst is reported to be active at temperatures above water loss. The

effect of water has suggested that Mn^{3+} (as $MnOOH$) is transformed to Mn^{4+} which was assumed to be the active site for O_2 adsorption, This assumption from did not agree conceptually with either the acid-base properties of the reactants (CO and O_2) or the relative basicity of hydrated Cu and Mn oxide surface [Kondrat *et al.*, 2011].

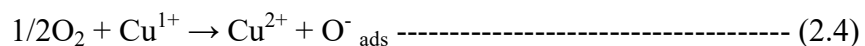
Hutchings and co-workers envisioned a coupled of dehydration reaction between hydrated Cu and Mn oxides. The acid-base properties of the reactants were used to support for the discussion. CO is basic and O_2 is acidic, it was expected that hydrated Cu oxide will dehydroxylate and hydrated Mn oxide will protonate to form water [Hutchings *et al.*, 1996]. This process would form a comparatively unstable Cu^{3+} cation but the Mn^{3+} would remain unchanged. The excess electron on $MnOO'$ would be transferred to Cu^{3+} generating Cu^{2+} [Irawan *et al.* 2015].



This equation was supported with the fact that Cu_2O and MnO_2 are active catalysts for CO oxidation. This suggestion was supported by Tanaka findings in that the maximum activity occurs for Cu mole fraction of 0.5 coincidental and the maximum Mn^{3+}/Mn^{4+} ratio [Tanaka *et al.*, 2003]. Solosona *et al.* [Solosona *et al.*, 2004] have attributed to the oxidation activity of $CuMn_2O_4$ to Mn^{4+} where:



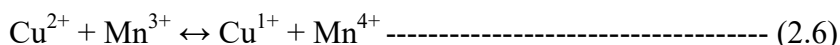
The promotion of Cu has further been linked to the reduction of O_2 :



The oxidation occurs by the process:



The resonance reaction system brings the catalyst back to the active state



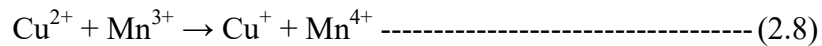
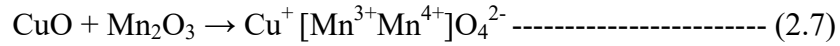
Hutchings and co-workers [Hutchings *et al.*, 1998] stated that if Equations 2.4, 2.5 and 2.6 applied, the deactivation of this catalyst system cannot be connected to the oxidation state of Cu or Mn as long as the redox couple remains active.

2.2 Mechanism of electron transfer in copper manganese oxides

Over the years, there has been much importance in Cu and Mn spinels. Remarkable crystallographic properties were expected due to the occurrence of the two types of Jahn Teller ions, Mn^{3+} and Cu^{2+} . In spite of the attention given to the subject, the sharing of the metal cations amongst tetrahedral and octahedral sites, as well as the valencies of the copper and manganese ions is still weakly understood [Ivanov *et al.*, 2015]. In 1958, Sinha and co-workers were amongst the first to report that the hopcalite spinel, CuMn_2O_4 , had a cubic structure. After consider X-ray intensities and bonding rules they proposed the formula, $\text{Cu}^+[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4$, where manganese was present in mixed oxidation states and its cations were present in an octahedral environment [Aldridge 2011]. Mirzaei, agreed and in 2003 published his own findings, proposing a configuration of $\text{Cu}^{2+}[\text{Mn}^{3+}]\text{O}_4$, based on the assumption that the local distortions caused by octahedral and tetrahedral Cu^{2+} balance for each other resulting in a macroscopic structure [Mirzaei *et al.*, 2003].

A variety of authors have reported that the complexity in preparing pure CuMn_2O_4 . A tetragonal spinel was obtained by involved heating to temperatures around 940°C . At lower temperatures, the cubic spinel phase was obtained but it was found to contain a significant quantity of impurities [Morales *et al.*, 2006]. Yap reported that the preparation of stoichiometric CuMn_2O_4 to be impossible at room temperature to mostly

confirm this theory. He recommended that a cubic configuration could only arise with excess copper ($x = 0.05$) for $\text{Cu}_{1+x}\text{Mn}_{2-x}\text{O}_4$. It indicated that tetrahedral Cu^+ and octahedral Mn^{4+} offer the steadiest environment in copper magnetite spinels [Yap *et al.*, 2018]. The reaction between Mn_2O_3 and CuO was accompanied by electron transfer.



The Cu^+ preferred a tetrahedral site due to its d^{10} configuration, forming stable sp^3 bonds. Whereas the two types of manganese cation, Mn^{3+} & Mn^{4+} that had $3d^4$ and $3d^3$ electronic configurations respectively, would be stabilized in octahedral sites through forming dsp^2 & d^2sp^3 hybrid bonds. As the fraction of O_H sites occupied by distorting cations (Mn^{3+}) was reduced, the mutual interface between the distorted O_H , responsible for parallel alignment was also reduced, randomizing the orientation and preserving the cubic symmetry [Papavasiliou *et al.*, 2005]. Further discrepancies arise in the literature when considering the valencies of the copper and manganese ions in hopcalite. A series of magnetic and structural investigations of CuMn_2O_4 lead to a number of researchers suggesting Cu and Mn to be the most stable configuration of the mixed oxide [Zaki *et al.*, 2009].

Others suggested that Cu^+ in the existence of Mn^{4+} was the most viable environment. Loeb and Good enough report the deficiency of deformation where distorting cations occupy a quarter of the O_H sites, with the phenomena being observed in manganites containing a mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ phase. With an increasing presence of Mn^{4+} in the crystals, The O^{2-} could form three p-bond orbitals and overlap with the three neighboring $\text{Mn}^{3+}/\text{Mn}^{4+}$ cations or form sp^3 hybrid orbitals (as in Cu_2O) where Cu-O was covalent [Goodenough and Loeb 1955]. The observed values of Cu-O and Mn-O

were intermediate between those considered from the covalent and ionic radii reported by Pauling. It indicating a resonating system where bonds were partially covalent and partially ionic [Pauling 1960]. The determination of the oxidation states of the components of hopcalite has also proved challenging to a number of other researchers. Investigations have shown that the ionization state of copper in copper manganite, CuMn_2O_4 , was different from that of copper in other iso-amorphous compounds such as CuCr_2O_4 and CuFe_2O_4 where it was Cu^{2+} . The Cr and Fe in these compounds were considered to be present as M^{3+} , where as in CuMn_2O_4 , the consensus of findings points to Mn^{4+} [Jones *et al.*, 2009].

This thesis is focused at developing a robust and reproducible preparation method aimed at synthesizing hopcalite based catalysts with increased catalytic activity and stability. It is expected that the active species produced will be able to rival the performance of the commercial catalysts available. The effect of ageing times and heat treatment will be probed, mainly in relation to the inclusion of other elements in to the hopcalite system, which was hoped a promotional and/or stabilizing effect on the activity. The mechanism of CO oxidation over the hopcalite catalysts have been raised in the literature in relation to the deactivation of hopcalite catalysts with time on stream and due to poisoning by water vapors and other species via blocking of surface active sites. Mechanistic insights will be offered both from steady state and transient response experiments encompassing the Temporal Analysis of Products (TAP) technique. The understanding of these parameters will be important to the design of experimental procedures involving precipitation as the method of catalyst preparation. A variety of preparation methods and characterization techniques will be used with the aim of producing the ultimate hopcalite-based CO oxidation catalyst.

2.3 Objectives of the present research work

Keeping in view the facts mentioned above, the objectives of the present study have been set as listed below:

- To develop low cost active hopcalite catalysts for oxidation of CO at a lower temperature
- To synthesize the catalyst precursors followed by calcination under different atmospheres of stagnant air, flowing air and reactive calcination in flowing CO-air mixture to obtain various CuMnOx catalysts
- To screen out various catalysts for identification of the most suitable one for CO oxidation
- To optimize AgCuMn₈Ox loading on γ -alumina support for CO oxidation
- To characterize the most suitable catalysts by various techniques such as low-temperature N₂ adsorption, XRD, SEM- EDX and FTIR
- To study the kinetics of CO oxidation over the most suitable supported AgCuMn₈Ox