



Mechanistic approach of CO oxidation over $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ system

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ABSTRACT

The compounds of $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ series with different Cu–Co compositions were synthesized by co-precipitation method and sintered at 500 °C for the formation of monophasic compounds. These were characterized by X-ray diffraction, IR spectroscopy, thermal analysis, BET surface area and scanning electron microscopy techniques. The effects of Cu–Co compositions on the catalytic activity for CO oxidation were investigated. The reaction was carried out in the temperature range from room temperature to 400 °C and also over some compounds prepared under different pH conditions. It is observed that the compounds prepared at pH 8.5 under basic condition showed higher activity than prepared at neutral pH. The attempts were made to correlate the other studies with the catalytic activity.

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1. Introduction

The development of carbon monoxide oxidation catalyst has become an important research topic during the last few decades. Gold and some noble metals dispersed on various oxides showed activity at sub-ambient temperatures [1–3]. Mixed metal oxide type catalysts, such as perovskites and spinels have been studied for CO oxidation and showed good catalytic activity [4–6]. However, the high cost of precious, rare earth metals and their sensitivity to sulfur poisoning have long motivated the search for substitute catalysts. The base metal catalysts deserve more attention for their significant activities and much lower cost. The mixtures of transition metal oxides have been widely studied in recent years. This type of study is quite useful in understanding the fundamental and technological aspects to provide a rational basis for the catalyst selection. Although this reaction has importance of its own, it has been studied as a model reaction to test the catalysts efficiency and to deduce important phenomenon in catalytic processes. Compounds belonging to tungstates family have been studied for various technological applications, and in particular copper and cobalt tungstates have received the wide attention because of their applications as scintillation detectors, gas sensors, catalysts and in electro-chromic systems [7]. However, no data is available in the literature for CO oxidation studies over metal tungstate compounds. In the present investigation, the catalytic CO oxidation activity on various compositions of copper and cobalt tungstates prepared at neutral and basic pH conditions were presented.

2. Experimental

2.1. Preparation

The $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ compositions ($x = 0.0, 0.3, 0.5, 0.7, 1.0$) were prepared by co-precipitation method. The respective metal nitrates and sodium tungstate of AR pure grade were taken in stoichiometric proportions and dissolved separately in distilled water to obtain a clear solution. Aqueous solutions were mixed and precipitated as metal tungstates at neutral pH. The precipitate was kept in ice cooled water for 1–2 h and then filtered and thoroughly washed with water to make them free from sodium ions. The precipitate was dried at 150 °C, homogenised well in an agate mortar and heated at 500 °C for 5 h.

The compounds CuWO_4 and CoWO_4 were also prepared with the same procedure as above with maintaining pH 8.5 using 1 N solution of NaOH. The solutions were mixed and precipitate metal tungstate in solution maintained at pH 8.5. It is expected to increase the basic sites on the surface of the catalyst by this process. These solids were dried at 150 °C for 1 h in air and then calcined at 500 °C for 5 h in a furnace.

2.2. Characterization techniques

Routine phase analysis was conducted with a ETAL APD 2000 diffractometer using the $\text{Cu K}\alpha$ radiation through Ni filter. The thermal analyses were carried out on TG-DSC (NETZSCH TG-DSC STA 409PC) in air at a heating rate of 10 °C/min. The sodium contamination in the catalysts prepared by co-precipitation method using NaOH was found out by employing atomic absorption spectrophotometer (AAS). IR analyses were performed using Shimadzu

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IR prestige21 series spectrophotometer, in the range of 400–1000 cm^{-1} . Diffuse reflectance spectra (DRS) were recorded on Shimadzu UV 2450 UV–Visible Spectrophotometer in the wavelength scan range of 400–800 nm. Surface areas of the compositions were measured using BET surface area analyzer by nitrogen adsorption method (SMART SORB 91 surface area analyzer). The surface morphology of the compounds was studied with scanning electron microscope (SEM) model (JEOL model 5800LV) with acceleration voltage 20 kV \times 1000 \times 2000 magnifications. A gold coating was deposited on the samples to avoid charging of the surface.

2.3. Catalytic tests

The catalytic activity for CO oxidation was tested using a fixed bed glass reactor in which around 1.5 g of the catalyst powder was supported between glass wool plugs. The reaction temperature was measured by chromel–alumel thermocouple dipped in the catalyst bed through a temperature controller. The activity was determined using a feed gas composition of 5% CO, 5% O₂ in nitrogen. The individual gas flow rates were controlled using flow meters and precision needle valves. The reactants and product composition were analyzed on-line by a gas chromatograph equipped with a thermal conductivity detector (TCD). The CO was prepared by standard procedure by formic acid disproportionation using sulfuric acid and was purified by passing through appropriate traps [6,8]. The N₂ and O₂ gases were used from commercial pure cylinders.

3. Results and discussion

3.1. X-ray diffraction and surface area

The formations of monophasic compositions were checked by recording the X-ray powder diffraction of all the samples. Fig. 1 shows the XRD patterns of the Cu_{1-x}Co_xWO₄ compounds prepared at 500 °C and the dhkl and 2 θ values are in good agreement as reported by ICDD data card. Metal tungstates MWO₄ (where M = Cu/Co) crystallized with the wolframite type of structure, having hexagonal closed packed oxygen atoms with certain octahedral sites filled by M²⁺ and W⁶⁺ cations in an ordered way [4,7,9–12]. Since the *d*-spacing of the intermediate compositions are not available in the literature, the values were compared with the end compositions.

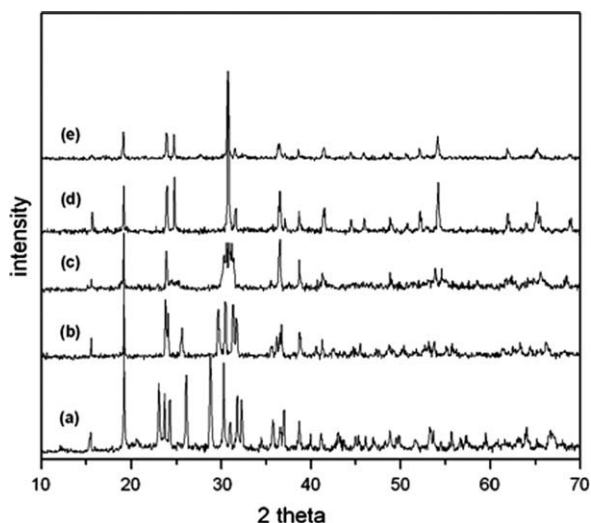


Fig. 1. X-ray powder diffraction pattern of Cu_{1-x}Co_xWO₄: (a) CuWO₄, (b) Cu_{0.7}Co_{0.3}WO₄, (c) Cu_{0.5}Co_{0.5}WO₄, (d) Cu_{0.3}Co_{0.7}WO₄ and (e) CoWO₄.

Table 1

Particle size, light of temperature and the reaction rate over the catalysts prepared at neutral pH.

Catalyst	Surface area (m ² /g)	Particle dimension by SEM (~nm)	Light off temperature [50% CO conversion] (T °C)	Rate at 150 °C (molecules m ⁻¹ s ⁻¹)
CuWO ₄	2.0	133	315	3.11 \times 10 ¹⁷
Cu _{0.7} Co _{0.3} WO ₄	2.3	123	335	2.71 \times 10 ¹⁷
Cu _{0.5} Co _{0.5} WO ₄	5.7	92	253	1.09 \times 10 ¹⁷
Cu _{0.3} Co _{0.7} WO ₄	8.8	62	136	0.71 \times 10 ¹⁷
CoWO ₄	8.6	46	323	0.72 \times 10 ¹⁷

The results obtained by BET surface area are shown in Table 1 and they are in the range 2.0–8.8 m²/g. The fall in surface area of CuWO₄ is due to the low melting point of the compound, as a result got sintered faster than the higher melting point materials.

3.2. Thermal techniques

In order to determine the calcination temperature of the precursors, TG–DSC studies of the precipitated compositions were carried out in the air at a heating rate of 10 °C min⁻¹. TG curve showed a weight loss of 8% up to 400 °C. Thus the weight loss was caused by the evaporation of residual water and followed by solid state diffusion reaction in the formation of monophasic compounds. Thus the compounds sintered at 500 °C for 5 h resulted in the formation of monophasic compounds.

3.3. FTIR analysis

The ABO₄ structure is known to be characterized by IR spectra in the region of 1000–400 cm^{-1} as shown in Fig. 2. In the IR spectra of mixed metal oxides, strong absorption bands were observed in the 900–400 cm^{-1} regions corresponding to the stretching vibrations of metal oxygen bond as seen in Fig. 2. The lower frequency band has been assigned to a deformation mode of WO₄ tetrahedra i.e. the W–O–W. The absorption bands with their maxima at 870–910 cm^{-1} can be assigned to the stretching mode of W–O bonds joins with WO₄ tetrahedra [13,14]. The frequency of these

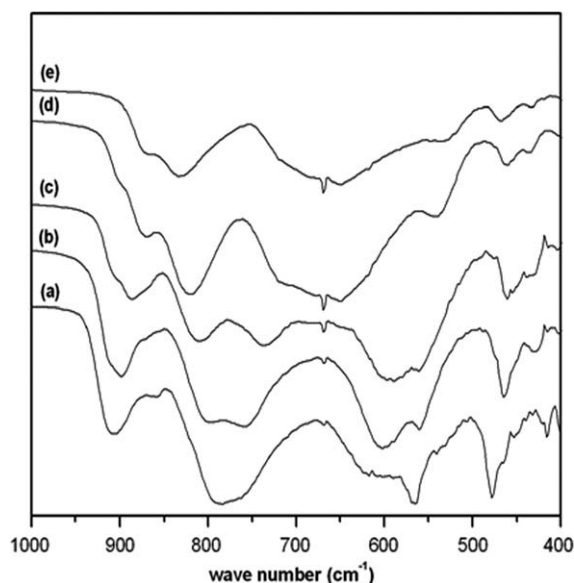


Fig. 2. The FTIR spectra of Cu_{1-x}Co_xWO₄ series where (a) CuWO₄, (b) Cu_{0.7}Co_{0.3}WO₄, (c) Cu_{0.5}Co_{0.5}WO₄, (d) Cu_{0.3}Co_{0.7}WO₄ and (e) CoWO₄.

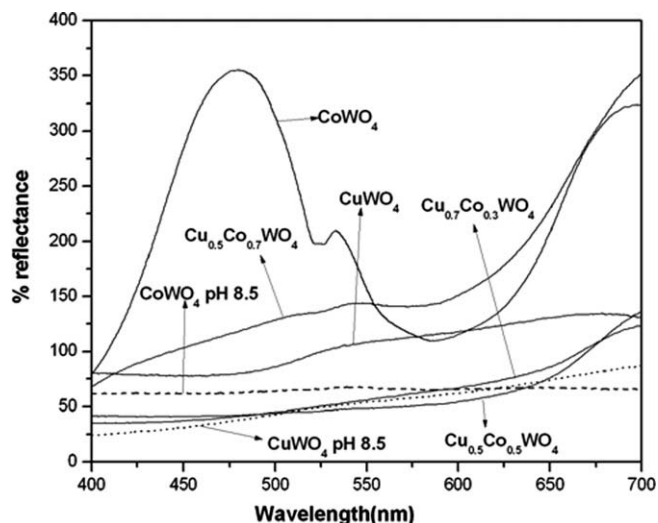


Fig. 3. Diffuse reflectance spectra of $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ compounds and of CuWO_4 , CoWO_4 prepared at pH 8.5.

bands has been related to the strength of the metal–oxygen covalency. It is observed that with the substitution of Co^{2+} in CuWO_4 , the strong absorption peak at 790 cm^{-1} gets gradually broadened for the compositions from $x = 0.3$ – 0.7 and shifted to a lower frequency. A broad absorption bands occurring at 780 – 800 cm^{-1} is due to Cu – O stretching. With the increase of Co the Cu – O stretching peak gets merged into Co – O stretching peak. The absorption bands occurring below 600 cm^{-1} can be due to the deformation modes of W – O bonds or the deformation modes of W – O – W bridges [15].

3.4. Diffuse reflectance spectroscopy

The diffuse reflectance spectra of $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ samples prepared by neutral pH were recorded at room temperature and are shown in Fig. 3. The spectra show no sharp drop of energy which conclude that they are not good semiconductors at room temperature. Some of these compounds show absorption bands indicating that they are coloured pigments. The CoWO_4 is a colour pigment when prepared under neutral pH condition and has shown two absorption bands in the region 450 – 550 nm . Whereas the compounds CuWO_4 and CoWO_4 prepared at pH 8.5 using NaOH solution are not coloured and also did not show any absorption

peaks as seen in Fig. 3. The spectra indicate that the compounds do not seem to be low band gap semiconductor materials at room temperature which is also confirmed by electrical resistivity measurements. The colours in some of these compounds are pH sensitive. However, X-ray pattern confirmed their formation prepared at neutral and basic pH conditions.

3.5. Surface morphology

The SEM images of the sintered $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ compounds were taken at 20,000 magnifications as shown in Fig. 4. The images of the particles are nearly spherical with crystallite size approximately in the range 50 – 100 nm . From these it can be inferred that increase in cobalt content leads to the formation of smaller particles and resulting to uniformity. As the CuWO_4 has melting point at around $925\text{ }^\circ\text{C}$, the sintering rate is higher and therefore, obtained higher particle size than other compounds. The compounds are found to be very fine polycrystalline materials. The particle dimensions are in good agreement with the surface area values.

3.6. CO oxidation

The catalytic activities of the compounds prepared at neutral pH were tested for CO oxidation. Fig. 5 shows the CO conversion against catalyst temperature for the above compounds. $\text{Cu}_{0.3}\text{Co}_{0.7}\text{WO}_4$ showed good activity, whereas $\text{Cu}_{0.7}\text{Co}_{0.3}\text{WO}_4$ and CoWO_4 showed lower activity as compared to the others. Although CoWO_4 shows higher surface area showed low activity. CoWO_4 is a coloured pigment when prepared in neutral pH and electrons are used for electronic transition resulting in less density of free electrons [16]. The low activity for $\text{Cu}_{0.7}\text{Co}_{0.3}\text{WO}_4$ is due to low surface area. But on $\text{Cu}_{0.3}\text{Co}_{0.7}\text{WO}_4$, the activity is found to be higher in spite of large cobalt content and this may be due to the higher surface area and also not coloured compound. The rate is calculated at the light off temperature and is shown in Table 1.

The CO oxidation studies of the compounds CuWO_4 and CoWO_4 prepared at pH 8.5 are also shown in Fig. 5. In this case the CuWO_4 shows 92% conversion at $400\text{ }^\circ\text{C}$ and CoWO_4 has 100% conversion at $180\text{ }^\circ\text{C}$. CoWO_4 is not a coloured when prepared at pH 8.5, hence there is no electronic transition as seen in Fig. 3. Compounds prepared at pH 8.5 in basic media certainly increase the density of basic sites on the surface, as a result more number of free electrons are available for O_2 adsorption [17] which facilitates the oxidation of CO at a lower temperature. The catalyst prepared at neutral pH exhibits lower basic sites [16]. From the above observations, we may conclude that both acidic and basic sites are essential in equal

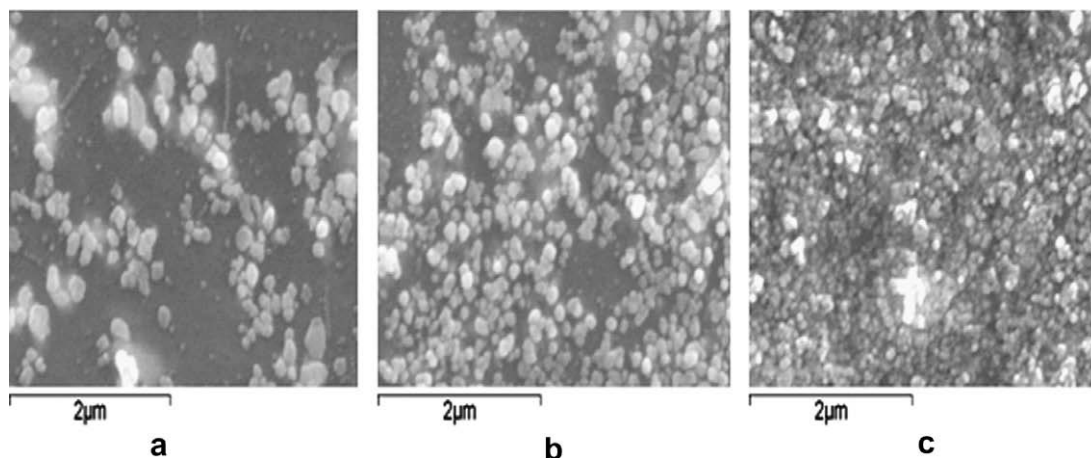


Fig. 4. SEM Photographs of the compounds prepared at pH 7.0: (a) CuWO_4 (b) $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$ and (c) CoWO_4 .

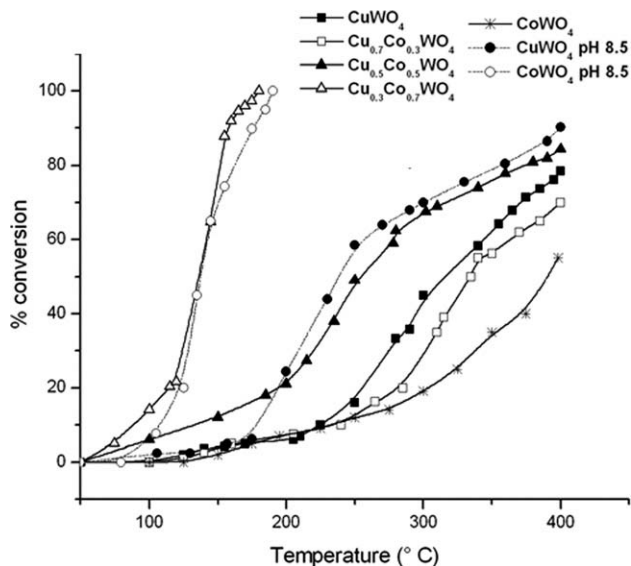
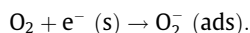


Fig. 5. Carbon monoxide conversion against catalyst temperature over $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ and of compounds prepared at pH 8.5.

ratio for CO oxidation. From CO oxidation studies carried out on catalyst prepared from both neutral and basic pH conditions, it is clear that the basic sites are capable of the activation of molecular oxygen species as follows [18]:



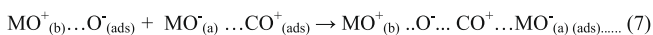
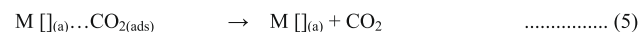
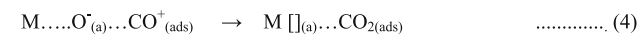
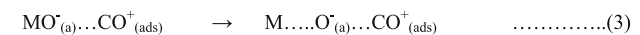
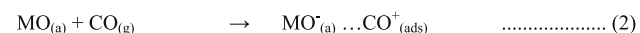
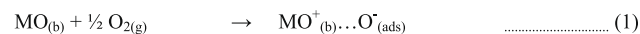
At the reaction temperature, the oxygen species O_2^- formed on the surface is an active species, which can react with CO to form CO_2 .

The CO chemisorptions resulting from the σ lone pair dative bond with metal ion, but no back donation from the metal 3d to the π^* orbital of carbon monoxide occurs. The influence of reticular oxygen on the interaction between CO and oxide surface was already suggested for alumina [19] and Co_3O_4 [20] which are consistent with a CO oxidation process. The strong interaction between carbon monoxide and the Lewis acidic metal ions may be attributed to bulk donation of electronic density from CO levels to surface states. The back donation was observed to involve the Lewis basic sites nearest to the CO carbon. If this is the case, the system should be stabilized by a configuration in which carbon monoxide adsorbs with the carbon end forming a certain angle with the perpendicular to the surface, i.e. the M–CO bond axis should not be perpendicular to the surface [19]. Moreover, when considering a real surface, the presence of defects, hydroxyl groups, etc have to be considered.

3.7. Model for CO– O_2 reaction

Many investigators have proposed the reaction mechanism for CO oxidation by oxygen. The proposed reaction mechanism is based on earlier data and the present experimental data. Reaction is presumed to proceed by Langmuir–Hinshelwood type mechanism. However there are few reports which show that the reaction also proceeds by Eley–Rideal type mechanism [8,21]. One of the possible reaction path ways may proceed in the following steps as shown in Scheme 1:

$\text{MO}(\text{a})$ and $\text{MO}(\text{b})$ indicate metal oxide acidic and basic active sites respectively of the mixed metal oxide catalysts, (g) is gas and (ads) is adsorbed species, whereas $\text{M}[\]$ is the reduced active site of the catalyst. Here, the acidic sites are defined as those sites which have affinity to accept the electrons from the adsorbing species and basic sites are those which have tendency to donate the



Scheme 1.

electrons to the adsorbates during the adsorption process. Adsorption of O_2 is preferred on the basic sites as seen in Eq. (1). In Eq. (2), CO gets adsorbed on metal oxide acidic sites by transfer of electron from carbon atom of CO to metal ion M of the oxide resulting in the formation of chemisorbed species. In the second step chemisorbed CO species give rise to chemisorbed CO_2 at reduced metal site with anion vacancy as CO is a reducing gas. Partially bonded CO_2 gets desorbed leaving the reduced metal oxide on the lattice in Eq. (5), which subsequently takes up oxygen from gas phase as shown in Eq. (6). Partially adsorbed CO_2 produced in Eq. (8) which subsequently gives metal oxide and carbon dioxide. Resultant chemisorbed species may interact with the reactive species forming normal metal oxide as well as metal oxide with adsorbed CO_2 . Adsorbed CO_2 species on metal oxide being unstable at a higher temperature undergoes desorption to regenerate MO and leaving CO_2 in the gas phase. The above reaction mechanism is one of the possible reaction path ways and in agreement with many investigations in some form or the other.

4. Conclusion

In this study, $\text{Cu}_{1-x}\text{Co}_x\text{WO}_4$ catalysts were prepared by co-precipitation method and tested for selective CO oxidation. The catalytic activities and properties in selective oxidation were found to be strongly influenced by the acidic and basic sites. The catalyst $\text{Cu}_{0.3}\text{Co}_{0.7}\text{WO}_4$ showed the higher activity due to surface area and the co-operative effect of copper and cobalt in the compound. The CoWO_4 prepared at pH 8.5 showed good activity for carbon monoxide oxidation in the presence of both acidic and more basic sites in the same catalyst. It has been found that the density of acidic and basic sites, surface area, number of unpaired electrons and surface lattice defects play an important role in CO oxidation.

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