CHAPTER VIII

CATALYTIC ACTIVITY OF

Cu-Cr/Al₂O₃ CATALYSTS FOR CO OXIDATION

Abstract

Cu and Cu-Cr based catalysts were prepared on γ-Al₂O₃ support to study the carbon monoxide oxidation activity and the resistance to severe thermal and hydrothermal deactivation. The effect of modification of alumina by the addition of CeO₂ or TiO₂ on the overall performance of the catalyst was also studied. In general, all Cu catalysts are more active than corresponding Cu-Cr catalysts. The activity and stability of the catalyst vary with respect to support as Al₂O₃-CeO₂ > Al₂O₃-TiO₂ > Al₂O₃. The promoting effect of these dopants could be explained in terms of the metal-dopant interactions.
8.1 INTRODUCTION

Supported noble metal catalysts form an important class of heterogeneous catalysts as they are extensively used for a variety of industrially applied reactions including petroleum reforming, organic hydrogenation and dehydrogenation reactions, deoxygenation reaction etc. High specific activity and the ability to work at milder conditions are the main attractions in using these catalyst systems in chemical industry. Major application of noble metal based catalysts is for the control of automobile emissions. A combination of Pt, Pd and Rh is used as the active component in three-way automobile catalyst for the simultaneous reduction of NO and oxidation of CO and hydrocarbons. Nowadays, noble metals are dispersed on monolith support for critical applications like automobile exhaust control, catalytic combustion etc where the catalyst is subjected to (i) high temperature, (ii) numerous poisons and (iii) fluctuating gas compositions.

Noble metal catalysts have also found application for the oxidation of carbon monoxide. The oxidation activity has been found to vary with respect to the active metal as Pd>Pt>Rh. However, a strict control of air/fuel ratio is required for such catalysts to function effectively. Furthermore, these catalysts are highly sensitive to impurities since only a low amount of metal is present in them. Besides, the factors like high cost, noble metal scarcity, low recycling rates and increased diversified usage of noble metals restrict the use of these catalysts. Mainly because of these disadvantages, attention has focused on the development of cheaper non-noble metal alternatives for the oxidation of carbon monoxide in the past few years.

Mehandjeev, Piperov and Bliznakov examined the possibility of replacement of noble metals with mixed oxides of Cu and Co and observed high oxidation activity at Cu/Co atomic ratio of 0.5, but poor poison resistance at lower Cu loading on the catalyst. Interestingly, copper chromite catalyst was claimed as an efficient non-noble metal catalyst for automobile exhaust control. This catalyst was also applied for CO oxidation, water gas shift reaction, selective oxidation of propylene, hydrogenation of carbonyl compounds and olefins and decomposition of alcohols.
From an industrial point of view, supported metal oxides are superior to unsupported systems on account of their improved stability and longer life. Alumina supported Cu-Cr catalyst was found to be as efficient as their unsupported counterparts for CO oxidation\textsuperscript{17}. In addition, the use of monolith supported Cu-Cr catalysts for the simultaneous NO\textsubscript{x} reduction and oxidation of carbon monoxide and hydrocarbons in catalytic converter was addressed in the literature\textsuperscript{18}. Efficient functioning of these catalytic systems depends, to a great extent, on the activity and stability of reaction sites on the surface. In Cu-Cr catalysts, Cu has been proposed as the main active species and Cr as a promoter, which reduces deactivation rates. However, some contradictions still exist about the nature of active sites in Cu-Cr based catalysts\textsuperscript{19,20}.

Although Cu-Cr catalysts have been studied extensively, only scant information is available on the suitability of such systems for the oxidation of carbon monoxide at lower temperatures. This study aims at the development of alumina supported Cu-Cr catalysts with improved low temperature oxidation efficiency by incorporating additives like CeO\textsubscript{2} and TiO\textsubscript{2}. Besides, special attention has been given to evaluate the effect of these dopants on the resistance against particle growth in severe thermal and hydrothermal conditions. The role of active metals in imparting activity and stability to the catalyst was investigated. Attempts have also been made to correlate the catalytic activity and stability with active metal dispersion and different crystalline phases present in the lattice.

8.2 Experimental

8.2.1 Materials

Details regarding various chemicals and other materials used in the present study are given in Chapter II.
8.2.2 Catalyst preparation

A brief account of the impregnation technique employed for the catalyst preparation is provided in Chapter II. Gamma alumina extrusions (3 mm dia. & 10 mm height, Surface area \(= 245 \text{ m}^2/\text{g}\)) were modified with \(\text{CeO}_2\) or \(\text{TiO}_2\) by impregnating with an aqueous solution of cerous nitrate or ammonium titanyloxalate respectively. They were dried at 120 °C for 6 hours and then calcined at 540 °C for 1 hour. Both Cu and Cu-Cr catalysts were prepared on \(\gamma\)-\(\text{Al}_2\text{O}_3\), \(\gamma\)-\(\text{Al}_2\text{O}_3\)-\(\text{CeO}_2\) and \(\gamma\)-\(\text{Al}_2\text{O}_3\)-\(\text{TiO}_2\) supports keeping copper concentration at 10 % and \(\text{Cr/Cu}\) mole ratio at around 2. Copper and chromium were incorporated from aqueous solutions of their nitrates by incipient wetness impregnation method. The wet extrusions were dried at 120 °C for 6 hours and then calcined at 500 °C for 2 hours.

8.2.3 Analytical Methods

Details of analytical methods and other characterization techniques are given in Chapter II.

8.2.4 Catalytic studies

The catalytic behaviour of the catalysts was studied by evaluating metal dispersion by \(\text{O}_2\) or \(\text{CO}\) chemisorption, \(\text{CO}\) oxidation activity and stability in thermal and hydrothermal conditions. These experiments are carried out at identical conditions so as to compare the results of various catalysts. The procedures employed for these measurements are as follows:

a) Oxygen chemisorption

Oxygen chemisorption was performed in a pulse microcatalytic reactor attached to thermal conductivity detector. A schematic representation of the apparatus is given in Figure VIII. 1 The samples were reduced at 300 °C for 30 minutes, switched over to helium and the temperature raised to and maintained at 310 °C for 10 minutes. The reactor was cooled to room temperature and then pulsed with oxygen. From the amount
of oxygen consumed, % metal dispersion was calculated assuming a stoichiometry of 1:1.

b) **CO Chemisorption**

CO chemisorption was carried out in the same pulse injection system used for oxygen chemisorption. The samples were reduced with hydrogen at 300 °C for 30 minutes and cooled to room temperature before injecting pulses of carbon monoxide. A stoichiometry of 1:1 was taken for evaluating the metal dispersion from the amount of CO adsorbed.

c) **CO oxidation activity**

CO oxidation was performed in a continuous flow test unit as represented in Figure VIII. 2. The oxidation activity of the catalysts was evaluated in the temperature range 150 °C-250 °C in a tubular reactor loaded with 3 cc of the catalyst. The reactant flow used was a mixture of 130 ml/minute dry air and 20 ml/minute carbon monoxide. The inlet and outlet concentrations of carbon monoxide and carbon dioxide formed during reaction were analysed in a GC with FID detector. Carbon monoxide and carbon dioxide were converted to methane before entering the detector using a microcatalytic methanator connected after Poropak Q column in Gas Chromatograph.

d) **Thermal and hydrothermal deactivation**

Catalyst samples were subjected to high temperature treatments at 700 °C and 800 °C for one hour and were evaluated for CO oxidation activity at 200 °C.

For hydrothermal deactivation, catalyst samples were kept at 300 °C in a nitrogen stream containing steam for 48 hours and then dried at 120 °C for one hour. The CO oxidation activity of these samples was measured at 200 °C. The continuous test facility shown in Figure VIII. 2 was used for the hydrothermal treatment of the catalysts.
Figure VIII. 1
Pulse microcatalytic reactor for chemisorption

Figure VIII. 2
Continuous flow test unit for CO oxidation
8.3 **RESULTS**

Chemical analysis of $\text{Al}_2\text{O}_3$-$\text{CeO}_2$ and $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ supports showed dopant concentrations of 6.2% CeO$_2$ and 4.8% TiO$_2$ respectively. Surface area of the alumina extrusions used for the catalyst preparation is 245 m$^2$/g and that of CeO$_2$ and TiO$_2$ modified alumina was found to be 226 m$^2$/g and 232 m$^2$/g respectively. Cu and Cr contents, BET surface area and pore volume of all the catalyst samples are given in Table VIII. 1.

Table VIII. 1

<table>
<thead>
<tr>
<th>Analytical, surface area and pore volume data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al$_2$O$_3$</td>
</tr>
<tr>
<td>Cu (wt %)</td>
</tr>
<tr>
<td>Cr (wt%)</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
</tr>
<tr>
<td>Pore volume (ml/g)</td>
</tr>
</tbody>
</table>

Analytical results indicate that Cu and Cr contents are quite close to the values targeted during preparation of the catalysts. The required quantities of metal salts were taken in the impregnating solution of volume just enough to fill the pores of the support so as to incorporate the components completely into it. In this way, % Cu in all the catalysts could be controlled at around 10 and Cr/Cu mole ratio at around 2. Surface area was found to reduce on incorporating the active ingredients into the support. In addition, surface area and pore volume of the catalysts containing Cr are lower than those of non-chrome catalysts.

Figure VIII. 3 shows the XRD patterns of Cu-Cr catalysts. The patterns indicate the presence of a number of crystalline phases including CuO, CuAl$_2$O$_4$, CuCr$_2$O$_4$ and
Figure VIII. 3

XRD spectra of Cu-Cr catalysts supported on (i) $\text{Al}_2\text{O}_3$, (ii) $\text{Al}_2\text{O}_3$-$\text{CeO}_2$ and (iii) $\text{Al}_2\text{O}_3$-$\text{TiO}_2$

(•) $\gamma$-$\text{Al}_2\text{O}_3$, (•) CuO, (•) CuCr$_2$O$_4$, (•) Cr$_2$O$_3$ (•) CuAl$_2$O$_4$ (•) CeO$_2$ (•) TiO$_2$
Cr$_2$O$_3$. The formation of such crystalline phases in Cu-Cr/Al$_2$O$_3$ catalyst was observed by previous workers also $^{17}$.

The oxidation activity is represented as the percentage conversion of carbon monoxide to carbon dioxide. These values at different temperatures are given in Table VIII. 2. Figure VIII. 4, a plot of % conversion against temperature, indicates the effect of temperature on the efficiency of the catalysts for carbon monoxide oxidation. Cu based catalysts are more active than those containing Cu and Cr as active components. Similar observation has been reported previously at low metal concentrations $^{21}$.

Cu and Cu-Cr catalysts on Al$_2$O$_3$-CeO$_2$ support showed substantial increase in activity than those supported on Al$_2$O$_3$ and Al$_2$O$_3$-TiO$_2$. For Cu/Al$_2$O$_3$-CeO$_2$, 100 % conversion was achieved at 210 °C whereas in the case of Cu-Cr/Al$_2$O$_3$-CeO$_2$, a temperature of 220 °C was required to get full conversion. TiO$_2$ incorporated catalysts also showed better performance than those prepared on alumina support, but not to the extent of those prepared on Al$_2$O$_3$-CeO$_2$. For Cu and Cu-Cr catalysts on Al$_2$O$_3$-TiO$_2$.

Table VIII. 2

Carbon monoxide oxidation data

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>150°C</th>
<th>175°C</th>
<th>200°C</th>
<th>225°C</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al$_2$O$_3$</td>
<td>9.0</td>
<td>23.4</td>
<td>59.3</td>
<td>84.8</td>
<td>95.2</td>
</tr>
<tr>
<td>Cu-Cr/Al$_2$O$_3$</td>
<td>6.9</td>
<td>18.6</td>
<td>49.7</td>
<td>75.2</td>
<td>88.3</td>
</tr>
<tr>
<td>Cu/Al$_2$O$_3$ -CeO$_2$</td>
<td>60.7</td>
<td>88.3</td>
<td>95.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Cr/Al$_2$O$_3$ -CeO$_2$</td>
<td>48.3</td>
<td>64.1</td>
<td>85.5</td>
<td>97.9</td>
<td></td>
</tr>
<tr>
<td>Cu/Al$_2$O$_3$ -TiO$_2$</td>
<td>32.4</td>
<td>62.8</td>
<td>78.6</td>
<td>99.3</td>
<td></td>
</tr>
<tr>
<td>Cu-Cr/Al$_2$O$_3$ -TiO$_2$</td>
<td>23.4</td>
<td>48.3</td>
<td>71.7</td>
<td>89.7</td>
<td></td>
</tr>
</tbody>
</table>
support, the conversion of carbon monoxide to carbon dioxide was 100 % at 225 °C and 240 °C respectively whereas those on undoped support showed full conversion only at temperatures above 250 °C. Thus the incorporation of additives like CeO₂ or TiO₂ reduces the reaction temperature. It is also evident that the activity of various catalysts increases with respect to support in the order Al₂O₃ < Al₂O₃-TiO₂ < Al₂O₃-CeO₂.

Metal dispersions obtained from oxygen and carbon monoxide chemisorption are given in Table VIII. 3 and the values are represented as bar chart in Figure VIII. 5. The data reveal that adsorption sites are more dispersed in Cu catalysts than in Cu-Cr catalysts and vary with respect to support as Al₂O₃ < Al₂O₃-TiO₂ < Al₂O₃-CeO₂. Metal dispersions with respect to CO chemisorption is much lower than those obtained by oxygen chemisorption, indicating poor affinity of the catalyst for CO.
Table VIII. 3
Cu dispersion data from oxygen and carbon monoxide chemisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Cu dispersion from O₂ chemisorption</th>
<th>% Cu dispersion from CO chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al₂O₃</td>
<td>37.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃</td>
<td>30.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Cu/Al₂O₃ -CeO₂</td>
<td>44.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃ -CeO₂</td>
<td>38.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Cu/Al₂O₃ -TiO₂</td>
<td>41.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃ -TiO₂</td>
<td>35.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Figure VIII. 5
Cu dispersion from oxygen and carbon monoxide chemisorption

The activity results of thermally and hydrothermally deactivated samples are given in Table VIII. 4. These results are represented in Figure VIII. 6 and VIII. 7 respectively. It is evident that the extent of deactivation on high temperature treatment is more for Cu based catalysts. Similarly, Cu catalysts have experienced severe deactivation than Cu-Cr
catalysts on hydrothermal treatment also. This observation indicates that the addition of chromium, despite reducing the activity, improves stability against particle growth, which is likely to occur at severe operating conditions.

Table VIII. 4
Activity of thermally and hydrothermally treated catalyst samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Conversion after TT</th>
<th>% Conversion after HTT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700 °C</td>
<td>% Loss</td>
</tr>
<tr>
<td>Cu/Al₂O₃</td>
<td>40.6</td>
<td>31.5</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃</td>
<td>37.2</td>
<td>25.2</td>
</tr>
<tr>
<td>Cu/Al₂O₃ -CeO₂</td>
<td>86.7</td>
<td>9.6</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃ -CeO₂</td>
<td>80.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu/Al₂O₃ -TiO₂</td>
<td>61.5</td>
<td>21.8</td>
</tr>
<tr>
<td>Cu-Cr/Al₂O₃ -TiO₂</td>
<td>59.8</td>
<td>16.6</td>
</tr>
</tbody>
</table>

TT = thermally treated  HTT = hydrothermally treated

Figures VIII. 6 and VIII. 7 afford a comparison of various Cu and Cu-Cr catalysts with respect to the support vis-a-vis resistance against thermal and hydrothermal deactivation. It can be observed that among various catalyst samples, deactivation rate is much less for that prepared on Al₂O₃-CeO₂. The resistance to thermal and hydrothermal sintering varies with respect to support as Al₂O₃ < Al₂O₃-TiO₂ < Al₂O₃-CeO₂. On the basis of above observation, it should be expected that CeO₂ and to a certain extent TiO₂ play an important role as structural promoter to minimise deactivation on severe thermal and hydrothermal treatments.
Figure VIII. 6
Effect of thermal deactivation on activity

Figure VIII. 7
Effect of hydrothermal deactivation on activity
8.4 DISCUSSION

Supported Cu based catalysts are generally more active for the oxidation of carbon monoxide than Cu-Cr catalysts. This observation is in agreement with previous reports on Cu-Cr catalysts\textsuperscript{21}. Lower activity exhibited by Cu-Cr catalysts can be attributed to its lower surface area and pore volume than those of Cu based catalysts. The lowering of surface area and pore volume could be due to the dilution of support and the filling of pores on introducing active components into the support. Furthermore, high Cu dispersion in Cu catalysts may also be a reason for their enhanced activity as Cu sites provide the main reaction centers for the oxidation of carbon monoxide.

CuO and CuAl\textsubscript{2}O\textsubscript{4} are the possible phases in Cu based catalysts, whereas CuCr\textsubscript{2}O\textsubscript{4} and Cr\textsubscript{2}O\textsubscript{3} are also identified in the XRD patterns of Cu-Cr catalysts. CuO and CuAl\textsubscript{2}O\textsubscript{4} phases have been reported to be present predominantly on the surface of Cu-Cr catalysts with Cu concentration less than 12%. These phases are more active for the oxidation of carbon monoxide as they are more reducible than CuCr\textsubscript{2}O\textsubscript{4}\textsuperscript{17}. However, in the case of Cu-Cr catalysts with high Cu concentration, weakly active CuCr\textsubscript{2}O\textsubscript{4} phase plays a major role in CO oxidation, as most of the Cu on the surface is available as CuCr\textsubscript{2}O\textsubscript{4}\textsuperscript{17}. Therefore, the higher activity of Cu catalysts used in the present study is due to the well dispersed Cu sites formed by the reduction of easily reducible CuO and CuAl\textsubscript{2}O\textsubscript{4} phases on the surface of alumina. But, only a low concentration of these phases are present in Cu-Cr catalysts due to the partial formation of inactive CuCr\textsubscript{2}O\textsubscript{4}\textsuperscript{22}.

Additionally, the chromium introduced may not enter fully into the alumina lattice, but stays on the surface as small crystallites of Cr\textsubscript{2}O\textsubscript{3}\textsuperscript{24}. XRD patterns show the presence of surface Cr\textsubscript{2}O\textsubscript{3} in Cu-Cr catalysts. This inactive surface species can cover the Cu sites so as to lower metal dispersion, adsorption capacity and hence activity.

It is obvious from the deactivation studies that Cu catalysts experience significant loss in activity than Cu-Cr catalysts on thermal treatment. Cu sites can be stabilized in the spinel structure of either CuAl\textsubscript{2}O\textsubscript{4} in Cu catalysts or CuCr\textsubscript{2}O\textsubscript{4} in Cu-Cr catalysts\textsuperscript{25}. 

197
CuAl₂O₄ is a partially inverse spinel with about 40% Cu ions in octahedral sites, whereas CuCr₂O₄ is a normal spinel with copper ions in tetrahedral sites. It appears that Cu ions are stabilized more in tetrahedral sites than in octahedral sites. Therefore, on high temperature treatment, CuAl₂O₄ in Cu catalysts may undergo drastic sintering while the formation of stable CuCr₂O₄ spinels in Cu-Cr catalysts reduces particle growth.

Water has been found to be not only an inhibitor for carbon monoxide oxidation with either oxygen or nitrogen oxides on Cu based catalysts but also a medium which facilitates particle growth. Cu catalysts are significantly affected on hydrothermal treatment than are Cu-Cr catalysts. This observation further shows the promoting effect of chromium in imparting stability for Cu sites via stable CuCr₂O₄ formation.

The CO oxidation activity of both Cu and Cu-Cr catalysts could be improved by the addition of dopants such as CeO₂ or TiO₂. However, CeO₂ is superior to TiO₂ in its ability to enhance the oxidation efficiency at lower temperatures. The promoting effect of dopants could be attributed to higher metal dispersion in the modified catalysts. Catalysts modified with CeO₂ have showed considerable improvement in dispersion as compared to that of catalysts containing TiO₂. It is interesting that similar trend is observed for activity or Cu dispersion on comparing promoted and unpromoted catalysts. Furthermore, these additives impart stability to resist particle growth in severe thermal and hydrothermal deactivation processes. The stability of both Cu and Cu-Cr catalysts varies with respect to support as Al₂O₃ < Al₂O₃-TiO₂ < Al₂O₃-CeO₂. The ability of CeO₂ and TiO₂ to enhance metal dispersion, catalytic activity and stability has been seen previously in supported noble metal catalysts.

The promoting effect of CeO₂ or TiO₂ could be interpreted in terms of the interactions between these additives and metal ions. The interaction between Group VIII metals and support has been of scientific and industrial interest. The unusual effect observed in a series of metal/oxide support systems is called "strong metal-support interaction" (SMSI). The SMSI in supported noble metal catalysts results in high metal dispersion, small crystallite size, high sorption and high relative activity.
Similar effects are also expected in the case of alumina supported Cu or Cu-Cr oxides. Several mechanisms and models have been proposed in the case of noble metal catalysts to explain the role of CeO$_2$ and TiO$_2$ in metal support interactions leading to enhanced activity and stability of the catalyst.

Earlier studies have provided some insight into the role of cerium oxide in increasing the catalytic activity.$^{35}$ Non-stoichiometry sets in rare earth oxides under reducing conditions leading to n-type semiconductivity. The activation energy for semiconductivity, which reflects the ease with which oxygen atoms can be removed from the lattice, has found to be very low for CeO$_2$. The formation of CeO$_{1.945}$ by evacuation followed by hydrogen treatment of CeO$_2$ at 450 °C has been reported.$^{36}$ A phase change has also been detected using X-ray diffraction patterns on the partial reduction of CeO$_2$. The reduced species can be oxidised back to CeO$_2$ with oxidising reactants. This redox property of CeO$_2$ plays a major role in enhancing the oxidation activity by providing parallel working sites$^{37}$ as given below

$$
2\text{CeO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{Ce}_2\text{O}_3
$$

$$
\text{Ce}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow 2\text{CeO}_2
$$

In a series of lanthanide oxides, CeO$_2$ is particularly active for both oxidation$^{38}$ and hydrogenation$^{35}$ reactions. The high activity has been attributed to the relative ease of oxygen vacancy formation and their involvement in the reaction mechanism. This redox behavior has also shown by TiO$_2$$^{34,39}$.

The electronic effects have also been considered to rationalize SMSI. As per this, the electronic interactions between the active metal atoms and reduced dopant ions at the dopant-metal interface account for the sorptive and catalytic changes observed$^{34,40}$. The role of CeO$_2$ in the phenomenon of increase of CO oxidation activity of alumina supported noble metal$^{41}$ and Cu catalysts$^{42}$ has been studied by EPR spectra. The enhanced CO oxidation activity observed for CeO$_2$ doped catalysts is due to the increased reactivity of $\text{O}_2^-$ radicals adsorbed in the coordination sphere of Ce$^{4+}$ ions. The
reactivity of these $O_2^-$ radicals can be explained in terms of the metal-dopant electronic interactions.

The work function of reduced CeO$_2$ is much lower than that of Cu metal and therefore electrons are transported to metal from the conduction zone of CeO$_2$ adjacent to it until the Fermi levels of both the solids are equalised. The interaction of CO with $O_2^-$ radicals leads to the formation unstable carbonate like anion intermediates on the catalyst. The high electron density on the metal enhances the rate of formation of this intermediate at the expense of transfer of electrons from the metal to the intermediate.

The reaction scheme can be represented as given below

$$O_2^- + CO + e^- \rightarrow CO_3^{2-}$$
$$CO_3^{2-} \rightarrow CO_2 + O^- + e^-$$

The reactivity of $O_2^-$ radicals lying deeper relative to the Fermi level i.e. located away from metal-dopant interface is low and the reaction with CO can occur as per the following reactions:

$$O_2^- + CO \rightarrow CO_2 + O^-$$
$$O^- + CO \rightarrow CO_2 + e^-$$

This mechanism explains that the higher reactivity of $O_2^-$ radicals at the metal-dopant interface leads to the enhancement of CO oxidation activity.

The migration of dopants onto the surface of active metal has also been suggested for explaining metal-dopant interactions$^{34,41}$. Partially reduced species of both CeO$_2$ and TiO$_2$ are able to migrate through or across the metal particles to cover some of their surface. In extreme cases metal particles can be totally immersed in the oxide support, which is termed as 'encapsulation'. As per this concept, the dopant not only shields the surface of active metal but also enters into electronic interaction with it, thus causing alterations in its catalytic properties.
A tentative model, called as "Vacancy interaction model", which involves the occupancy of oxygen ion vacancies in the oxide support by noble metal atoms has been proposed to account for the metal support interactions. The vacancies are called as nests and the process is called nesting. The same phenomenon may be applicable for Al₂O₃-CeO₂ or Al₂O₃-TiO₂ supported Cu atoms obtained on reducing the catalyst. In the case of metal atoms located on an ideal surface i.e. without oxygen vacancies, only a weak interaction exists between the metal atom and the surface. In such cases the atoms will easily migrate on the surface until they coalesce to form large crystallites. This results in the loss of metal dispersion, adsorption capacity and hence catalytic activity. In contrast to the above case, the metal atoms supported on reducible oxides like CeO₂ and TiO₂ can occupy the oxygen vacancies formed on the surface during reduction. This phenomenon increases active metal dispersion and surface area, maintains high sorptive capacity and hence results in high catalytic activity. In addition, the metal atoms are expected to be stabilized more when occupied in these vacancies as compared to those on the ideal surface.

Ceria appears to enhance the noble metal dispersion, thermal stability and activity in automotive catalysts. However, the important feature of ceria in oxidation reaction is the ability to store oxygen, which in turn helps to maintain required oxygen stoichiometry during lean operating conditions. Furthermore, the migration of oxygen molecules weakly adsorbed on ceria to the metallic site has been reported to facilitate CO oxidation on Rh/Ceria catalyst. However, further work will be needed to find the role of this spill over process in oxidation reactions over ceria promoted Cu-Cr catalysts.

8.4 SUMMARY AND CONCLUSION

The overall performance of alumina supported Cu-Cr catalysts shows its suitability for use as an effective non-noble metal system for the oxidation of carbon monoxide. The role of chromium is to stabilise the Cu sites against thermal and hydrothermal deactivation, but it marginally reduces the carbon monoxide oxidation activity as compared to that of non-chrome catalyst. The stability imparted by Cr is particularly important for high temperature operation
of such catalysts. The additives like CeO$_2$ or TiO$_2$ can enhance not only the ability of the catalyst to withstand severe thermal and hydrothermal conditions but also the low temperature oxidation efficiency. These dopants not only improve Cu dispersion and facilitate reaction on it but also provide parallel reaction sites, and thus render the catalyst to be effective even at low temperatures. In all respects, CeO$_2$ is much superior to TiO$_2$ as a promoter in Cu-Cr catalysts for CO oxidation. The exact nature of Cu-CeO$_2$ interactions and how these interactions influence catalyst performance are aspects that need to be the foci of future investigations.