

# Versatile Applications of Metal/Mixed Metal Oxides as Catalyst

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## ABSTRACT:

The metal oxides / mixed metal oxides have various applications as catalyst, photocatalyst, sensors, superconductors, adsorbent, ceramics, fuels, antifungal agents and have large number of applications in medicines. These metal / mixed metal oxides play a very important role in day to day human life. Today metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior. In this article an attempt has been made to focus on their applications as catalyst in various chemical reactions.

**Keywords:** Metal oxides, Mixed metal oxides, catalyst, chemical reactions

## INTRODUCTION:

The metal elements are able to form a large diversity of oxide compounds [1]. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or Nano arrays with special properties with respect to those of bulk or single practice species [2-6]. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. These comprises the structural characteristics, namely and lattice symmetry and cell parameters [7]. Bulk oxides are usually stable systems with well-defined crystallographic structures. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in  $\text{TiO}_2$ ,  $\text{VO}_x$ ,  $\text{Al}_2\text{O}_3$  or  $\text{MoO}_x$  oxides [8-10].

## Catalyst :

Metal/Mixed metal oxides have wide applications as catalyst some of the important uses are described here. Morales *et al.*[11] synthesized manganese iron or nickel mixed oxide catalysts ( $\text{MnFe}$  or  $\text{MnNi}$ , respectively). A detailed description of the bulk and surface structure of each system was achieved by means of measurements of specific surface area, XRD, XPS, FT-IR, and Mossbauer spectroscopies. The characterization results show that  $\text{MnNi}$

catalysts are formed as  $\text{NiMnO}_3$  and  $\text{Ni}_6\text{MnO}_8$  mixed oxides besides a little amount of  $\text{Mn}_2\text{O}_3$ . In contrast,  $\text{MnFe}$  catalysts consist of an oxide mixture ( $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_5\text{O}_8$ ) forming incipiently a solid solution. The catalytic activity was evaluated in the combustion of propane and ethanol, selected as model volatile organic compounds. Luca and coworkers [12] used the tar reforming catalytic activity of iron and nickel based catalyst supported on alkaline-earth oxides  $\text{CaO}$ ,  $\text{MgO}$  and calcined dolomite [a  $(\text{CaMg})\text{O}$  solid solution] investigated in a fixed bed reactor operating at temperatures ranging from 650 to 850 °C; Toluene and 1-methyl naphthalene were used as model compounds for tar generated during biomass gasification. Mostafa *et al.* [13] synthesized the iron nickel oxide catalysts were prepared using co-precipitation procedure and studied for the conversion of synthesis gas to light olefins. In particular, the effects of a range of preparation variables such as  $[\text{Fe}]/[\text{Ni}]$  molar ratios of the precipitation solution, precipitate aging times, calcination conditions, different supports and loading of optimum support on the structure of catalysts and their catalytic performance for the tested reaction were investigated. It was found that the catalyst containing 40%Fe/60%Ni/40wt% $\text{Al}_2\text{O}_3$ , which was aged for 180 min and calcined at 600 °C for 6 h was the optimum modified catalyst. Guan *et al.* [14] prepared the calcined scallop shell (CS) applied for the adsorption and decomposition of biomass -derived tar. In this study, steam reforming of tar derived from pruned apple branch over CS was investigated in a fixed bed at 650 °C. It was found that CS had good activity for the steam reforming of tar to produce synthesis gas (syngas), and was able to be recycled. To promote the gas production efficiency, iron or nickel was supported on the CS, and used for the reforming of tar. The effect of heating rate on the gas production rate was investigated, and it was found that reduced iron or nickel supported CS showed better activities under the condition of rapid heating. Iron or nickel-based catalyst in its oxide state was also investigated for the reforming of tar. Huang *et al.* [15] showed the iron-doped nickel oxide films application as oxygen evolution catalysts in the photoelectrochemical production of hydrogen from solar energy. The effects of processing parameters on the film properties, such as overpotential, composition, surface morphology and preferred orientation, were investigated. The electrochemical experiment, structural and compositional measurements indicate that the relative lower substrate temperature, higher RF power, higher working pressure and oxygen content are necessary to gain lower overpotential. M. Rahman and coworkers [16] carried out Nickel oxide on alumina aerogel catalysts are known to convert propylene into acrylonitrile through the interaction with nitric oxide (nitridation). For a  $\text{NiO}/\text{Al}_2\text{O}_3$  aerogel catalyst, with Ni:Al ratio 1:1, the activity decreases by about 20% over a 3-h run. Simultaneously, a carbon deposit is observed on the catalyst which results from the cracking of hydrocarbons and from the Boudouard reaction of generated carbon monoxide. Addition of water vapor into the feed slows down the deactivation process by promoting the water-gas shift reaction without affecting the activity. Addition of a basic component like magnesia (0.2 Mg:0.8 Ni) to the  $\text{NiO}/\text{Al}_2\text{O}_3$  aerogel catalyst also enhances the stability by retarding the cracking reactions. Lihong Huang *et al.* [17] studied Iron-doped  $\text{LaNiO}_3$  catalysts with a perovskite structure prepared via self-combustion and tested in auto-thermal reforming (ATR) of ethanol. Characterizations of temperature-programmed surface reaction (TPSR), X-ray diffraction (XRD), physical  $\text{N}_2$  adsorption, and temperature-programmed reduction (TPR) were carried out. The results indicate that  $\text{LaNiO}_3$  perovskite structure was successfully formed via self-combustion. With iron-doping

in  $\text{LaNiO}_3$ , the perovskite structure still remains, in the form of solid solution  $\text{La}(\text{Ni}, \text{Fe})\text{O}_3$ , where iron is reducible and the nickel-iron alloy forms after the reduction. In addition, the surface area of the iron-doped samples increased. Morozova *et al.* [18] discovered the  $\text{NiO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  samples from various backgrounds and used as precursors of the catalysts for CO hydrogenation. The effect of the initial microstructure of oxides on the morphological peculiarities and catalytic properties of the newly formed catalysts was studied using transmission electron microscopy and in situ XRD combined on-line with gas-chromatographic analysis. Tsoncheva and coworkers [19] found that several SBA-15 type mesoporous silicas, where different means of surfactant removal have been used, have been modified by copper and iron oxide, and tested as catalyst for methanol decomposition. The materials were thoroughly characterized by nitrogen physisorption, X-ray diffraction, Mossbauer spectroscopy and temperature programmed reduction with hydrogen. The different means of template removal results in SBA-15 materials different in mesopore size and degree of micro porosity. These parameters have a strong influence on the reductive and catalytic properties of the obtained composite materials. Natter *et al.* [20] studied cluster models for sites on the  $\{111\}$  surface of  $\text{Fe}_3\text{O}_4$  and used to study the strength of bonding of water-gas shift intermediates using density functional theory. Three site models were used, representing an unpromoted catalyst, a catalyst where copper cations substitute for iron cations below the surface and a catalyst where copper cations substitute in the surface. The strengths of bonding of oxygen, carbon dioxide, dissociated water and dissociated formic acid were all observed to decrease by less than  $20 \text{ kJ mol}^{-1}$  when copper substituted below the surface, but they decreased by  $60\text{--}80 \text{ kJ mol}^{-1}$  when copper substituted in the surface of the catalyst. Tsoncheva and coworkers [21] examined mixed copper and iron modified MCM-41 mesoporous silica with various Cu/Fe ratio characterized by  $\text{N}_2$  physisorption, X-ray diffraction (XRD), transmission electron micrographs (TEM), X-ray photoelectron spectroscopy (XPS), Mossbauer spectroscopy and temperature programmed reduction with hydrogen. Their catalytic properties in methanol decomposition to CO and  $\text{H}_2$  are investigated and compared with that of the corresponding mono-component materials. The catalytic behavior of bi-component materials are discussed based on the nature of the catalytic active sites. Kustov *et al.* [22] worked on vanadyl, copper and iron oxide catalysts supported on conventional  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and sulphated –  $\text{TiO}_2$  and  $\text{ZrO}_2$ . These catalysts were characterized by elemental analysis,  $\text{N}_2$ -BET, XRD, and  $\text{NH}_3$ -TPD methods. The influence of potassium oxide additives on the acidity and activity in NO selective catalytic reduction (SCR) with ammonia was studied. The absolute activity of the samples does not vary significantly depending on the nature of the active metal and the acidic properties of the support used, seem to be influenced mainly by the concentration of active metal. Zhang *et al.* [23] produced the metal–silica interaction and catalytic behavior of Cu-promoted Fe–Mn–K/ $\text{SiO}_2$  catalysts were investigated by temperature-programmed reduction/desorption (TPR/TPD), differential thermogravimetric analysis, in situ diffuse reflectance infrared Fourier transform analysis, and Mossbauer spectroscopy. The Fischer–Tropsch synthesis (FTS) performance of the catalysts with or without copper was studied in a slurry-phase continuously stirred tank reactor. The characterization results indicate that several kinds of metal oxide–silica interactions are present on Fe–Mn–K/ $\text{SiO}_2$  catalysts with or without copper, which include iron–silica, copper–silica, and potassium–silica interactions. Simona and coworkers *et al.* [24]

utilized the properties of copper-based pillared clays (Cu-PILC) have been studied and compared with those of the analogous iron-based clays (Fe-PILC) in the wet hydrogen peroxide catalytic oxidation (WHPCO) of model phenolic compounds (p-coumaric and p-hydroxybenzoic acids) and real olive oil milling wastewater (OMW). These two catalysts show comparable performances in all these reactions, although they show some differences in the rates of the various steps of reaction. In particular, Cu-PILC shows a lower formation of oxalic acid (main reaction intermediate) with respect to Fe-PILC. K. Eguchi *et al.* [25] cauterized the reduction process of copper-iron spinel oxide, which is active for steam reforming of dimethyl ether after mixing with alumina, has been investigated by a transmission electron microscope (TEM), scanning TEM (STEM), and energy dispersive X-ray (EDX) analyzer. The catalyst preparation was started from formation of well-sintered  $\text{CuFe}_2\text{O}_4$  by calcination in air at  $900^\circ\text{C}$ . After reduction of  $\text{CuFe}_2\text{O}_4$  with hydrogen at  $250^\circ\text{C}$ , metallic copper grains were developed on reduced spinel surface by the phase separation from the oxide. Strong chemical interaction between deposited Cu and reduced spinel oxide was expected from their intimate interfacial contact and lattice matching. Han *et al.* [26] evaluated a series of Cu-Fe bimetal amidoxime polyacrylonitrile (PAN) fiber complexes with different molar ratios of  $\text{Cu}^{2+}$  to  $\text{Fe}^{3+}$  ions prepared using a simple exhaustion method, and characterized using FTIR, DRS and XPS, respectively. They were tested as the heterogeneous Fenton catalysts for Rhodamine B degradation with  $\text{H}_2\text{O}_2$  in the dark and under visible light irradiation. The results indicated that Cu-Fe bimetal amidoximated PAN fiber complexes could more effectively catalyze the dye degradation in water than Fe amidoximated PAN fiber complex, especially in the dark. Riz *et al.* [27] checked the oxidative dehydrogenation of n-butane to butenes over iron-zinc oxide catalysts. X-ray diffraction (XRD), temperature-programmed reduction (TPR) and Mossbauer spectroscopy were used to try to identify the catalytically active phase. It was found that the presence of a zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) phase with a spinel structure yields high selectivity to butene's. Nam and coworkers [28] analyzed the hydrogenation of carbon dioxide to hydrocarbon over iron catalysts. Studies were carried out in a fixed bed reactor under pressure of 10 atm and temperature of 573 K. Iron catalysts promoted with V, Cr, Mn and Zn prepared by precipitation method were adopted in the present study. The catalysts were characterized by XRD, carbon dioxide chemisorption and  $^{57}\text{M}$ össbauer spectroscopy. The hydrocarbons were formed directly from carbon dioxide over iron catalysts. Rethwisch *et al.* [29] studied supported iron oxide and zinc oxide samples as water-gas shift catalysts at temperatures from 620 to 720 K. The supports studied were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{ZnO}$  and Na-mordenite. The catalytic activity of all supported iron samples was significantly lower than that of magnetite ( $\text{Fe}_3\text{O}_4$ ). It is suggested that whereas magnetite functions as a catalyst via an oxidation-reduction pathway, all supported iron and zinc oxide samples operate via an associative mechanism for the water-gas shift. The catalytic activities of the supported samples decreased as the acidity of the support or the electronegativity of the support cations increased. Mirzaei and coworkers [30] find out the effect of a range of preparation variables such as the precipitate ageing time and  $[\text{Fe}]/[\text{Co}]$  molar ratio of precipitation solution on the composition and morphology of iron-cobalt oxide catalysts prepared using a co-precipitation method is described and the optimum preparation conditions were identified with respect to the catalyst activity for the Fisher-Tropsch reaction. The effect of different promoters along with loadings of optimum support and promoter on the



activity and selectivity of the 40%Fe/60%Co as an optimum molar ratio are studied and it was found that the catalyst containing 40%Fe/60%Co/15 wt%SiO<sub>2</sub>/1.5 wt%K which aged for 2 h, is an optimum modified catalyst for the conversion of synthesis gas to ethylene and propylene. Mizaei and coworkers [31] synthesized iron cobalt oxides and studied for the conversion of synthesis gas to light olefins. In particular, the effect of a range of preparation variables such as the precipitate ageing time and [Fe]/[Co] molar ratio of the precipitation solution were investigated in detail. The preparation procedure and also the optimum preparation conditions were identified with respect to the catalyst activity for the hydrogenation of carbon monoxide. The results are interpreted in terms of the structure of the active catalyst and it has been generally concluded that the catalyst containing 40% Fe/60% Co – on molar basis – and aged for 2 h, is the most active catalyst for the conversion of synthesis gas to ethylene and propylene. Zhou Weiqing *et al.* [32] investigated a new heterogeneous catalyst, lead–zinc double oxide. It had been prepared for the synthesis of diphenyl carbonate (DPC) by transesterification of dimethyl carbonate (DMC) and phenol. The effects of preparation method, calcination temperature, precursor and molar ratio of Pb/Zn on the catalytic activity have been investigated. XRD, TPR and atomic absorption spectroscopy were employed for the catalyst characterization. The results show that Pb<sub>3</sub>O<sub>4</sub> is the main active species, and that amorphous ZnO plays a role as the promoter. Wang *et al.* [33] studied nanoparticle zinc-titanium oxide materials prepared by the aerogel approach. Their structure, surface state and reactivity were investigated. Zinc titanite powders formed at higher zinc loadings possessed a higher surface area and smaller particle size. X-ray photoelectron spectroscopy (XPS) revealed a stronger electronic interaction between Zn and Ti atoms in the mixed oxide structure and showed the formation of oxygen vacancy due to zinc doping into titania or zinc titanate matrices. The 8–45 nm aerogel particles were evaluated as catalysts for methanol oxidation in an ambient flow reactor. Carbon dioxide was favorably produced on the oxides with anion defects. Machado *et al.* [34] described the immobilization of anionic iron (III) porphyrin (FePor) family on zinc hydroxide chloride (ZHC). The FePor immobilization was performed at room temperature under magnetic stirring, under air atmosphere, of each complex ethanol solution and the ZHC solid support suspension. Pollard *et al.* [35] synthesized Georgeite basic copper carbonate mineral, can be synthesized in aqueous solutions from copper salts. It has now been shown that a zincian georgeite (i.e. georgeite with some substitution of copper by zinc) is formed by precipitation with sodium carbonate in copper-zinc systems. Conversion of zincian georgeite to a malachite phase in an aqueous medium occurs more slowly than the equivalent conversion of pure copper georgeite. The possibility of georgeite formation as a precursor to malachite in the manufacture of copper/zinc catalysts is discussed: it is suggested that the blue/green color transition seen during the ageing of precipitated copper/zinc catalyst precursors can be attributed to the conversion of georgeite to malachite. Pollard *et al.* [36] studied four new bimetallic model precursors of copper-zinc oxide catalysts for methanolization. The new compounds were characterized by elemental analysis, IR spectroscopy, and thermal analysis under dynamic conditions. Li and coworkers [37] discovered the doping effect of potassium permanganate on the performance of a copper/zinc oxide/alumina catalyst for methanol synthesis. It was found that doping with potassium permanganate appreciably enhanced the activity of the catalyst. The optimum nominal dosage of potassium permanganate was found to be 6.0 mol.%. The precursors and the

calcined, reduced and syngas-treated catalysts undoped and doped with potassium permanganate were characterized by X-ray photoelectron spectroscopy and X-ray-induced auger transition, powder X-ray diffraction, atomic absorption spectroscopy and temperature programmed oxidation. Sengupta *et al.* [38] developed mixed oxides of copper and zinc by thermal decomposition of the coprecipitates obtained from mixed metal nitrate solutions by addition of ammonium bicarbonate (series AB<sub>n</sub> and hydroxide series AM<sub>n</sub>). These were characterized by diffuse reflectance spectroscopy and electron spin resonance spectroscopy. It was found that in series AB<sub>n</sub> appreciable dissolution of Cu<sup>2+</sup> ions in the zinc oxide matrix had occurred and in this solid solution the Cu<sup>2+</sup> ions occupied distorted octahedral sites. Inui and coworkers [39] investigated the effect of ultrasonic treatment on methanol synthesis activity of a copper/zinc/aluminum oxide catalyst has been investigated. It has been found that intonation of the suspension during co-precipitation and aging steps appreciably enhanced the activity of the catalyst and along with the increase of the frequency of the ultrasound, the enhancement grew stronger. It has also been revealed that this enhancement is due to the promotion of the ultrasound for the formation of the hydrotalcite – like phase in the precursor of the catalyst. Saito *et al.* [40] developed the role of metal oxides such as Ga<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> contained in Cu/ZnO-based ternary catalysts for methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> was classified into two categories: to improve the Cu dispersion and to increase the specific activity. Huang *et al.* [41] found that hydrogen production resulting from the partial oxidation of methanol (POM) was investigated using copper-zinc-supported gold catalysts. The influence of oxygen concentration on activity and initiation temperature (T<sub>i</sub>) over Au<sub>4.3</sub>CZ (ca. 4.3 wt.% Au, 32.3 wt.% Cu and 63.4 wt.% Zn) catalysts was compared with CZ (ca. 31.7 wt.% Cu and 68.3 wt.% Zn) catalysts. The Au<sub>4.3</sub>CZ catalyst was able to react at temperatures lower than 195 °C, while CZ catalyst could not be initiated without pre-activation. Astier *et al.* [42] examined the new vanadium-copper-zinc and vanadium-copper or copper-zinc complex compounds prepared with variable Cu/ (Cu+Zn) atomic ratios with a theoretical (Cu+Zn)/V ratio of 1 by the reaction of ammonium vanadate with mixtures of copper and/or zinc ammonia complexes. The catalysts obtained from the reduction of these new compounds were systematically analyzed by the B.E.T. method and the surface copper concentration was determined by titration with nitrous oxide decomposition. Ethanol was dehydrogenated into ethanol only (selectivity of 100%) at 190°C under both dynamic and differential conditions. Suarez *et al.* [43] worked on the influence of ammonia and nitric oxide oxidation on the selective catalytic reduction (SCR) of NO by ammonia with copper/nickel and vanadium oxide catalysts, supported on Titania or alumina. In the SCR reaction, the VTi catalyst had a higher activity than VAl at low temperatures, while the CuNiAl catalyst had a higher activity than CuNiTi. A linear relationship between the reaction rate of ammonia oxidation and the initial reduction temperature of the catalysts obtained by H<sub>2</sub>TPR showed that the formation rate of NH<sub>3</sub> species in copper/nickel catalysts would be higher than in vanadium catalysts. Bianco *et al.* [44] discovered the selective reduction of NO<sub>x</sub> with ammonia on alumina-supported copper catalysts. It is shown to be effective when O<sub>2</sub> or NO<sub>2</sub> are present in the feed. Under steady state conditions, the presence of NO<sub>2</sub> in the feed stream increases the overall rate of reduction of NO<sub>x</sub> and simultaneously reduces its dependence on the oxygen concentration. A maximum in activity is found for a molar inlet ratio NO<sub>2</sub>/NO ≈ 1. It has also been observed that the stoichiometry of the process is a

function of the reaction temperature, with a secondary  $\text{NH}_3$  oxidation reaction appearing at temperatures above 500 K.

## CONCLUSION:

Above mentioned literature shows wide applications of metal /mixed metal oxides as catalyst in various reactions like iron oxide and zinc oxide samples as water-gas shift catalysts at temperatures from 620 to 720 K. The supports studied were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{ZnO}$  and Na-mordenite. The catalytic activity of all supported iron samples was significantly lower than that of magnetite ( $\text{Fe}_3\text{O}_4$ ). It is suggested that whereas magnetite functions as a catalyst via an oxidation-reduction pathway, all supported iron and zinc oxide samples operate via an associative mechanism for the water-gas shift. The catalytic activities of the supported samples decreased as the acidity of the support or the electronegativity of the support cations increased. So, metal/mixed metal oxides have broad applications as catalyst in various chemical reactions.

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