

Transition Metal Nano materials in Catalysis

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ABSTRACT:

The Transition 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 transition metal / mixed metal oxides play a very important role in day to day human life. Today transition 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: TransitionMetal oxides, Mixed metal oxides, chemical reactions, catalyst

INTRODUCTION:

The transition metals and their compounds are used as catalysts in chemical industry and in battery industries. Besides, these compounds can be used in formation of interstitial compounds and alloy formation. The transition metals have the special properties of formation of colored compounds and show magnetic properties. Metals of d-block elements are used for many industrial applications. They behave as catalysts, super conducting materials, sensors, ceramics, phosphors, crystalline lasers etc. Size-induced structural distortions associated with changes in cell parameters have been observed, for example, in nanoparticles of NiO, Fe₂O₃, ZrO₂, MoO₃, CeO₂ and Y₂O₃. As the particle size decreases, the increasing number of surface and interface atoms generates stress/ strain and concomitant structural perturbations [1-5].

The second important effect of size is related to the electronic properties of the oxide. In any material, the nanostructure produces the so-called quantum size or confinement effects which essentially arise from the presence of discrete, atom-like electronic states. From a solid-state point of view, these states can be considered as being a superposition of bulk-like states with a concomitant increase in oscillator strength [6]. Additional general electronic effects of quantum confinement experimentally probed on oxides are related to the energy shift of electronic levels and optical bandgap [7-8]. Structural and electronic properties drive the physical and chemical properties of the solid, the third group of properties influenced by size in a simple classification. In their bulk state, many oxides have wide band gaps and a low reactivity [9]. A decrease in the average size of an oxide particle does in fact change the magnitude of the band gap [10-11], with strong influence in the conductivity and chemical reactivity [12-13]. Surface properties are a somewhat particular group included in this subject have great

importance in chemistry. Solid-gas or solid-liquid chemical reactions can be mostly confined to the surface and/or sub-surface regions of the solid.

Catalyst:

Orsini and coworkers [14] utilized the reduction of NO with H₂ on copper nickel and chromium – nickel catalysts. Both CuNi and CrNi catalysts were prepared by impregnation on Al₂O₃ pellets. Dry-pressed catalysts, CrNi with Al₂O₃ powder were formed with several catalysts containing the NiCr₂O₄ spinel. A pressed nickel oxide catalyst was highly active for the reduction of NO while impregnated nickel oxide was much less active. Copper oxide and chromium oxide were relatively inactive. Addition of small amounts of copper to impregnated nickel oxide improved the activity of the latter catalysts, but above about 24 atomic percent copper, activity decreased with increase in copper content. The activity of the pressed chromium – nickel catalysts increased with increase in nickel content. Chakrabarti *et al.* [15] characterized catalytic reduction of nitric oxide with ammonia was studied by use of Girdler's G-22 (barium promoted copper chromite) and T-312 (nickel oxide and copper oxide on gamma alumina) catalysts inside a Carberry type stirred tank reactor. Helium was used as the carrier gas. The nitric oxide and ammonia concentrations in the feed varied from 550 to 1400 ppm and 700 to 7900 ppm, respectively. Temperature levels were from 177 to 316°C. Gas flow rates ranged from 200 to 300 l.h⁻¹. Empirical kinetic expressions for both catalysts were developed which adequately represent the experimental results. Fuentes *et al.* [16] evaluated nickel or copper-based catalysts obtained from hydrosulfite-like precursors in this work, in order to find catalysts able to work at intermediate temperatures (200–350°C) in water gas shift reaction (WGSR). Samples based on nickel (or copper), aluminum and zinc were obtained by co-precipitation, characterized by several techniques and evaluated in WGSR. Zinc caused changes in the cell parameters of hydrosulfite-type structure, which determined the structural and textural properties of calcined samples. For all catalysts, zinc oxide was detected. In the case of nickel-based hydrosulfites, aluminum cations were incorporated into nickel oxide lattice, hindering reduction; however, the addition of zinc decreased this effect. For copper-based samples, aluminum entered into copper oxide lattice and the copper reduction decreased with the increase of zinc amount in solids. After calcination, copper catalysts showed lower specific surface areas than nickel ones. Khadiri and Astier [17] checked a series of well-defined nickel, copper and nickel copper molybdenum complex compounds isomorphous of the ammonium thiaminetetra nickel pentamolybdate were prepared. The characterization of the catalysts obtained by reduction in hydrogen of these precursors is difficult but the use of the chemisorptive decomposition of nitrous oxide together with the reactions of benzene hydrogenation and propanol decomposition make possible an estimation of the surfaces atomic copper nickel ratio. Youn *et al.* [18] analyzed metal oxide-stabilized mesoporous zirconia supports (M–ZrO₂) with different metal oxide stabilizer (M = Zr, Y, La, Ca, and Mg) prepared by a templating sol–gel method. 20 wt.% Ni catalysts supported on M–ZrO₂ (M = Zr, Y, La, Ca, and Mg) were then prepared by an incipient wetness impregnation method for use in hydrogen production by auto-thermal reforming of ethanol. The effect of metal oxide stabilizer (M = Zr, Y, La, Ca, and Mg) on the catalytic

performance of supported nickel catalysts was investigated. Ni/M–ZrO₂ (M = Y, La, Ca, and Mg) catalysts exhibited a higher catalytic performance than Ni/Zr–ZrO₂, because surface oxygen vacancy of M–ZrO₂ (M = Y, La, Ca, and Mg) and reducibility of Ni/M–ZrO₂ (M = Y, La, Ca, and Mg) were enhanced by the addition of lower valent metal cation. Hydrogen yield over Ni/M–ZrO₂ (M = Zr, Y, La, Ca, and Mg) catalyst was monotonically increased with increasing both surface oxygen vacancy of M–ZrO₂ support and reducibility of Ni/M–ZrO₂ catalyst. Among the catalysts tested, Ni catalyst supported on yttria-stabilized mesoporous zirconia (Ni/Y–ZrO₂) showed the best catalytic performance. Narciset *al.* [19] discussed ZnO-supported Ni and Cu as well as bimetallic Co-Ni and Co-Cu catalysts containing 0.7 wt.% sodium promoter in the ethanol steam-reforming reaction at low temperature (523–723 K), using a bioethanol-like mixture diluted in Ar. Monometallic ZnO-supported Cu or Ni samples do not exhibit good catalytic performance in the steam-reforming of ethanol for hydrogen production. Copper catalyst mainly dehydrogenates ethanol to acetaldehyde, whereas nickel catalyst favors ethanol decomposition. Komatsu and coworkers [20] find out the catalytic activity of pure, doped nickel oxide, and mixtures of nickel oxides with different dopants was investigated by the reaction of carbon monoxide oxidation. The incorporation of lithium ions in the oxide enhanced the activity and the addition of indium lowered the activity. The activity of mixtures increased to several times greater than would be predicted by simple additive effect of single doped catalysts. Derazet *al.* [21] synthesized alumina-supported NiO catalysts, promoted with 0.14–3 wt.% ZnO prepared by impregnation and then calcined at 400, 600, and 800 °C for 4 and 40 h. The phase analysis, surface and catalytic properties were investigated by using XRD technique, nitrogen adsorption at -196 °C, and oxidation of CO by O₂ at 200–300 °C, respectively. The results obtained reveal that ZnO doping of Ni/Al mixed oxides followed by calcination at 400 or 600 °C for 4 h brought about slight increase in their specific surface area, which decreased progressively by increasing the calcination temperature of doped solids to 800 °C for 4 and 40 h. CO oxidation activity over NiO/Al₂O₃ mixed solids increased by treatment with ZnO followed by heating at 400 or 600 °C for 4 h, and then decreased by increasing the calcination temperature to 800 °C for 4 and 40 h. Zhuang and coworkers [22] used by using a thermal gravimetric balance reactor and a temperature-programmed reaction technique, it was found that carbon deposition on cerium oxide-containing nickel catalysts was decreased in both the induction and the constant carbon growth periods. Meanwhile the catalysts-maintained activity for the steam reforming reaction. Based on this and our previous research a model for the promoting effect of cerium oxide is proposed. Aai et al. [23] followed the results of a leaching kinetics study of spent nickel oxide catalyst with sulfuric acid. The effects of spent catalyst particle size, sulfuric acid concentration, and reaction temperature on Ni extraction rate were determined. The results obtained show that extraction of about 94% is achieved using –200+270 mesh spent catalyst particle size at a reaction temperature of 85 °C for 150 min reaction time with 50% sulfuric acid concentration. The solid/liquid ratio was maintained constant at 1:20 g/ml. The leaching kinetics indicate that chemical reaction at the surface of the particles is the rate-controlling process during the reaction. The activation energy was determined as about 9.8 kcal/mol, which is characteristic for a surface-controlled process. Zoo *et al.* [24] prepared the pre-reforming of commercial liquefied petroleum gas (LPG) was investigated over Ni–CeO₂

catalysts at low steam to carbon (S/C) molar ratios less than 1.0. It was found that the catalytic activity and selectivity depends strongly on the nature of the support and the interaction between Ni and CeO₂. The Ni–CeO₂/Al₂O₃ catalysts, which were prepared by impregnating boehmite (AlOOH) with an aqueous solution of cerium and nickel nitrates, exhibited the optimal catalytic activity and remarkable stability for the steam reforming of LPG in the temperature range of 275–375 °C. The effects of CeO₂ loading, reaction temperature and S/C ratio on the catalytic behavior of the Ni–CeO₂/Al₂O₃ catalysts were discussed in detail. Mucka *et al.* [25] showed the catalytic activities and some physio-chemical properties of NiO-ZnO catalysts prepared by precipitation of mixtures of carbonates and nitrates of both metals and subsequent calcination have been tested before and after irradiation, using the decomposition of hydrogen peroxide as a test reaction. A mutual influence of both oxides and their sensitivities to ionizing radiation have been proved. Busca *et al.* [26] carried out the urea hydrolysis method to prepare well-crystallized Ni-Co-Zn-Al Layered Double Hydroxides to be used as precursors of mixed oxide catalysts for the Ethanol Steam Reforming (ESR) reaction. The calcination of the layered precursors gives rise to high surface area mixed oxides, being actually a mixture of a rock salt phase (NiO), a wurtzite phase (ZnO) and a spinel phase. The steam reforming of ethanol has been investigated over these catalysts after calcination at 973 K in flow reactor experiments. All these catalysts are active for ESR. At 820 K the selectivity to hydrogen increases with cobalt content. The most selective catalyst is the Ni-free Co-Zn-Al mixed oxide essentially constituted by a single spinel type phase Zn_{0.55}Co_{0.45}[Al_{0.45}Co_{0.55}]₂O₄. Hao Yang *et al.* [27] reported the application of an inexpensive and easily-prepared lead oxide-manganese oxide catalyst combined with Nafion (designated as Nf/PbMnOx) as a highly efficient air-cathode for a zinc-air battery. Mechanistic study of the reduction of O₂ for Nf/PbMnOx in alkaline aqueous solution using rotating ring/disk electrode voltammetry, and also an electrochemical approach using a wall-jet screen-printed ring disk electrode has been verified. Hubicki and Wojcik [28] synthesized that platinum has been widely applied in catalytic industry and the recovery of noble metals from industrial wastes becomes an economic issue. The laboratory studies of platinum (IV) microquantities removal from 1 M aluminum, copper, iron, nickel and zinc chloride solutions in 0.1 M hydrochloric acid solutions on the anion exchanger Duolite S 37 of the functional secondary and tertiary amine groups were carried out. For this anion exchanger the fraction extracted values (%E, Pt(IV)) as well as the sorption isotherms were determined depending on the kind of aqueous phase and phase contact time. Majumdar *et al.* [29] used the thermal decomposition of the oxalates of zinc, nickel and iron(II) have been reexamined from a fresh experimental approach. Differential thermal analysis (DTA) and thermogravimetry (TG) of the individual oxalates and of mixtures of zinc oxalate with either nickel/iron oxalate or products of decomposition of the latter two, were carried out in air in sample cells made of different materials (Pt, Al, Al₂O₃, Ni). The information gathered from thermo analytical experiments, together with information derived from specific chemical tests for the evolution of carbon monoxide during decomposition, chemical analyses, XRD and stoichiometric and thermochemical considerations helped to specify some of the inadequately explained features of the courses and kinetics of decomposition of the metal oxalates. Yadav and Kharkara [30] followed liquid phase hydrogenation of a series of nitriles, namely,

benzonitrile, butyrotirle, cinnamonitrile and crotononitrile over and has been investigated and the activities of the catalysts have been correlated with the structure of the catalysts on the basis of frontier orbital energy levels. Bridieret *al.* [31] studied the partial hydrogenation of propyne over copper-based catalysts derived from Cu–Al hydrotalcite and malachite precursors and compared with supported systems (Cu/Al₂O₃ and Cu/SiO₂). The as-synthesized samples and the materials derived from calcination and reduction were characterized by XRF, XRD, TGA, TEM, N₂ adsorption, H₂-TPR, XPS, and N₂O pulse chemisorption. Catalytic tests were carried out in a continuous flow-reactor at ambient pressure and 423–523K using H₂:C₃H₄ ratios of 1–12 and were complemented by operando DRIFTS experiments. The propyne conversion and propene selectivity correlated with the copper dispersion, which varied with the type of precursor or support and the calcination and reduction temperatures. Tanseem Gul Kaziet *al.* [32] showed the pathogenesis of some heart diseases has been associated with changes in the balance of certain trace elements. We examined the association of iron, copper and zinc between biological samples (scalp hair, whole blood and urine) and mortality from myocardial infraction (MI) patients of (first, second and third heart attack). Kozłowski *et al.* [33] discovered metal ions, especially with high chemical activity (e.g. redox-active Cu and Fe) must be carefully managed in biological systems. The “uncontrolled” activity, e.g. catalysis of Fenton-like reactions by ions like Cu(I) or Fe(II), is so damaging for the biological milieu that right from their entry, metal ions need to be strictly controlled until they arrive at their storage site. Ferraris and Sergio De Rossi *et al.* [34] developed the behavior of Cu-ZnO catalysts in propene hydrogenation at 323 K has been investigated in order to gain information as to whether or not a synergic effect due to ZnO on the activity of copper is present. With this aim, two different series of catalysts were prepared by coprecipitation at (A) variable or (B) constant (≈ 8) pH. The whole composition range from CuO/ZnO 100:0 to 0:100 was covered in preparation A, while only copper-rich samples (CuO/ZnO $\geq 67:33$) were prepared from method B. Chemisorption experiments of hydrogen and propene on samples reduced with hydrogen at 473 K point to the presence of adsorption sites in binary samples different from those existing in single components, that are influenced by the outgassing temperature. Shimomura *et al.* [35] investigated copper oxide-zinc oxide-alumina catalysts for methanol synthesis and kneading methods for comparison of catalytic activity, physical properties, and estimation of the effective surface area by carbon monoxide chemisorption. The coprecipitated catalysts, which are already industrially employed, have higher catalytic activities than the kneaded ones, the optimum chemical composition being around Cu:Zn:Al = 60:35:5 (atom%) in both cases. The total pore volume, the mean pore radius, and the porosity of the coprecipitated catalysts were three to four times larger than those of the kneaded ones. The pore-size distribution ranges from 50 to 5000 Å for the coprecipitated catalysts and from 40 to 10,000 Å for the kneaded ones. The former is equivalent to the copper and zinc oxide values in an individual state, while in the latter the values change in the composite form, with 80- and 20-Å mean particle sizes, respectively. The crystallite size of the composition with a higher catalytic activity after reduction was about 100 Å both for zinc oxide and copper in the coprecipitated catalysts and 170–180 Å for copper and 270–280 Å for zinc oxide in the kneaded ones. From these facts it is proposed that a finely mixed state in the oxidized precursor has its origin

during the coprecipitation process. T.Tsoncheva *et al.* [36] worked on nanosized copper ferrites were prepared by thermal method from the corresponding hydroxide carbonate precursors varying the temperature of synthesis. The phase composition of the obtained materials was characterized by XRD, Mossbauer spectroscopy, DSC and TPR analysis. Their catalytic properties were tested in total oxidation of toluene and methanol decomposition to CO and hydrogen. K.Faungnawakiet *al.* [37] discussed dimethyl ether steam reforming (DME SR) was performed over composite catalysts of copper ferrite spinel (CuFe_2O_4) and alumina for hydrogen production, applicable to fuel cell. The composite catalysts both with and without pre-reduction were active for DME SR when the pre-reduced catalyst exhibited higher initial activity, but longer activation process was observed for the composite catalyst without pre-reduction. DME conversion and hydrogen production significantly depended on gas hourly space velocity (GHSV) and reforming temperatures (T_r). DME conversion (>95%), H_2 production rate ($\sim 50 \text{ mol kg}_{\text{cat}}^{-1} \text{ h}^{-1}$), and H_2 concentration (ca. 73%) were achieved at T_r of 350 °C and GHSV of 1500 h^{-1} . Yen – Chun Liu *et al.* [38] worked on copper ferrite Nano powders were successfully synthesized by a microwave-induced combustion process using copper nitrate, iron nitrate, and urea. The process only took a few minutes to obtain CuFe_2O_4 nanopowders. The CuFe_2O_4 powders specific surface area was 5.60 m^2/g . Moreover, these copper ferrite magnetic Nano powders also acted as a catalyst for the oxidation of 2,3,6-trimethylphenol to synthesize 2,3,5-trimethylhydroquinone and 2,3,5-trimethyl-1,4-benzoquinone for the first time. On the basis of experimental evidence, a rational reaction mechanism is proposed to explain the results satisfactorily. M.M.Rashad *et al.* [39] discussed cubic copper ferrite CuFe_2O_4 Nano powders have been synthesized via a hydrothermal route using industrial wastes. The synthesis conditions were systematically studied using statistical design (Box–Behnken Program) and the optimum conditions were determined. The results revealed that single phase of cubic copper ferrite powders can be obtained at different temperatures from 100 to 200 °C for times from 12 to 36 h with pH values 8–12. The crystallite size of the produced powders was in the range between 24.6 and 51.5 nm. The produced copper ferrite powders were appeared as a homogeneous pseudo-cubic-like structure. A high saturation magnetization (M_s 83.7 emu/g) was achieved at hydrothermal temperature 200 °C for 24 h and pH 8. Photocatalytic degradation of the methylene blue dye using copper ferrite powders produced at different conditions was investigated. A good catalytic efficiency was 95.9% at hydrothermal temperature 200 °C for hydrothermal time 24 h at pH 12 due to high surface area (118.4 m^2/g). Shou-Quing Liu *et al.* [40] worked on a magnetic species was synthesized in a 100 mL Teflon-lined stainless steel autoclave at 180 °C for 10 h. The synthesized species was characterized by powder X-ray diffraction, transmission electron microscopy, scanning electronic microscopy, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy and vibrating sample magnetometry at room temperature. The results showed that the synthesized species was nickel ferrite nanoparticles with diameters of approximately 10 nm. The nanoparticles exhibited a photo-Fenton catalytic feature for the degradation of rhodamine B in the presence of oxalic acid. The effects of pH, oxalic acid concentration, and dosage of the catalyst, on the degradation rates of the dyes were examined. Niyaz Mohammad Mahmoodi *et al.* [41] discussed photocatalytic ozonation of dyes with copper ferrite (CuFe_2O_4) nanoparticle (CF nanoparticle)

prepared by co-precipitation method was investigated. Reactive Red 198 (RR198) and Reactive Red 120 (RR120) were used as dye models. The characteristics of CF nanoparticle were studied using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). UV–Vis and ion chromatography (IC) analyses were employed to study of dye degradation. The effect of operational parameters on dye degradation such as CF nanoparticle dosage, pH, dye concentration and salt (inorganic anions) was studied. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediates. Wichaidponhanet *al.* [42] worked on tetragonal copper ferrite (CuFe_2O_4) nanofibers were fabricated by electrospinning method using a solution that contained poly(vinyl pyrrolidone) (PVP) and Cu and Fe nitrates as alternative metal sources. The as-spun and calcined CuFe_2O_4 /PVP composite samples were characterized by TG-DTA, X-ray diffraction, FT-IR, and SEM, respectively. After calcination of the as-spun CuFe_2O_4 /PVP composite nanofibers (fiber size of 89 ± 12 nm in diameter) at 500°C in air for 2 h, CuFe_2O_4 nanofibers of 66 ± 13 nm in diameter having well-developed tetragonal structure were successfully obtained. The crystal structure and morphology of the nanofibers were influenced by the calcination temperature. N. Tsubokawa *et al.* [43] worked on the oxidations of alcohols with copper(II) salts mediated by 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO) moieties immobilized on ultrafine silica and ferrite surface were investigated. Based on the above results, the oxidations of alcohols were considered to proceed as follows: alcohols are oxidized with oxoammonium moieties on silica and ferrite surface, which were formed by the reaction of surface TEMPO moieties with copper(II) salts, and oxoammonium moieties on the surface itself are reduced to the corresponding hydroxylamine moieties after the oxidation. Then the hydroxylamine moieties are oxidized with copper(II) salts to regenerate TEMPO moieties on the surface. For example, in the case of the oxidation of benzyl alcohol, Silica-TEMPO was recycled about 45 times. Silica-TEMPO and Ferrite-TEMPO were readily recovered from reaction mixture by centrifugation.

CONCLUSION:

Above mentioned literature shows wide applications of transition metal /mixed metal oxides as catalyst in various reactions like cubic copper ferrite CuFe_2O_4 Nano powders have been synthesized via a hydrothermal route using industrial wastes. The synthesis conditions were systematically studied using statistical design (Box–Behnken Program) and the optimum conditions were determined. The results revealed that single phase of cubic copper ferrite powders can be obtained at different temperatures from 100 to 200°C for times from 12 to 36 h with pH values 8–12. The crystallite size of the produced powders was in the range between 24.6 and 51.5 nm. The produced copper ferrite powders were appeared as a homogeneous pseudo-cubic-like structure. A high saturation magnetization (M_s 83.7 emu/g) was achieved at hydrothermal temperature 200°C for 24 h and pH 8. Photocatalytic degradation of the methylene blue dye using copper ferrite powders produced at different conditions was investigated. So, transition metal/mixed metal oxides have broad applications as catalyst in various chemical reactions.

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