Versatile Applications of Metal/Mixed Metal Oxides as Adsorbents

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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 Adsorbents in various chemical reactions.

Keywords: Metal oxides, Mixed metal oxides, chemical reactions, Adsorbents

INTRODUCTION:

Many metal oxides display acid/ base properties. Oxide materials can contain Bronsted and Lewis acid/base sites. Bronsted acid (A) and base (B) interactions consists of the exchange of protons as $HA+B = A + HB^+$. Lewis acidity is characteristic of ionic oxides and practically absent in covalent oxides. The strongest Lewis and oxides are Al_2O_3 and Ga_2O_3. As a rule, the stronger the Lewis acid, the few available sites (amount) due to the higher level of surface hydroxylation. As mentioned, because Lewis acidity is mostly associated to oxides with ionic character, Lewis basicity is mostly associated to oxides with ionic character, Lewis basicity is mostly associated with them. This means that the stronger the Lewis acid sites, the weaker the basic sites and vice versa. On the contrary, most of the ionic metal oxides do not carry sufficiently strong Bronsted acidity to protonate pyridine or ammonia at room temperature although the more acid of them can do it higher temperatures. In spite of this, the surface OH groups of most ionic oxides have a basic more than acid character. Covalent low-valent nonmetal oxides (SiO_2, GeO_x, Bo_x) also show quite weak Bronsted acid and properties. Finally, strong Bronsted acidity appears in oxides of elements with formal valence five or higher (WO_3, MoO_3, N_2O_5, V_2O_5 and S-containing oxides). Zinc oxide presents the wurtzite structure and displays a high covalent Zn-O bond [1]. ZnO is a wide band gap semiconductor extensively studied due to its intrinsic properties but with a limited industrial use as a UV-blocker in sun lotions [2], as a component in mixed oxide varistors [3], as a catalyst/ photocatalyst [4]. Additionally, forthcoming applications are envisaged as a gas sensor, solar cell and or / non-linear optical systems [5]. Of particular interest is the fact that ZnO can display novel nanostructures (nanoring's, Nano springs, Nano helices, and nanobots'), not typically observed in other oxides, due to the polar characteristics of their surface [6]. Surface and quantum size effects have been described as responsible of compressive strain and band gap blue shift in nanostructured ZnO nanoparticles. However, surface effects and particularly, non-stoichiometry and the presence of hydrogen (forming part ort no of hydroxyls) seem persistent phenomena with larger influence in the oxide properties when comparing with quantum – alone. Although acoustic phonons are dominated by quantum confinement, optical phonons and visible (yellow/green) luminescence display properties mostly related to the presence of defects and/or hydrogen impurities without significant chemical/ physical sensibility to confinement [7]. Chemical properties seem also enhanced by the nanostructure but again a critical role of oxygen vacancies and hydroxyl radicals is noticed [8]. There also been also a lot of work concerning ZnO-based mixed oxides mostly by doping with Mg, Mn and Cd in order to modulate the band gap of the oxide [9].

Adsorbents:

Metal / Mixed metal oxides have wide application as Adsorbents. Some of them are described here**.**Quan *et al.* [10] synthesized removal of Copper from aqueous solution using iron-containing adsorbents derived from methane fermentation sludge. Iron-containing adsorbents prepared from methane fermentation sludge (MFS) were characterized by N_2 adsorption, XRD, SEM, EDX, pH determination and elemental analysis. The desorption studies were also performed and the mechanisms of Cu(II) adsorption was proposed. The results indicated that the adsorbent obtained at 700^0C for 1 h in a steam atmosphere possessed the highest capability for Cu (II) adsorption. The invisibility of copper adsorption on the iron containing adsorbents is attributed to the formation of strong bonds between Cu (II) and the iron (hydro) oxides. The adsorbent can be applied to remove copper from water or soil by fixation onto the surface. Wang *et al.* [11] used Removal of impurities from copper electrolyte with adsorbent containing antimony. A new adsorbent was synthesized possesses not only the properties of common adsorbents, but also special merits of its own. The paper presents the results of adsorbent synthesis, characterization, regeneration, and metal ion separation. The feasibility of utilizing this adsorbent for copper electrolyte purification has been examined. Garces *et al.* [12] followed a new method for study of the adsorption function of an adsorbent on an adsorbent, applied to the study of the adsorption, applied to the study of the adsorption function of isopropyl alcohol on a zinc oxide catalyst 11. Quantitative treatment of the data. The sorbent's sorption capacity at breakthrough increased with the sulfidation temperature reaching 87% of the theoretical value for desulphurization at 400^0C. A deactivation model that considers the activity of the solid reactant was used to fit the experimental data. Good agreement between the experimental breakthrough curves and the model predictions was obtained.

Stein Kolfe [13] Prepared Characterization and properties of iron oxide coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. Thermodesorption curves of isopropyl alcohol from a zinc oxide catalyst which were given in Part I have been analyzed under the assumption that the Langmuir isotherm for a heterogeneous surface is a valid model. From visual inspection of the deposition curves five sets of adsorption sites were assumed. K. Osseo Asare and D.W. Fuerstenav [14] discovered Adsorption phenomena in hydrometallurgy, the uptake of copper nickel and cobalt by oxide adsorbents in aqueous ammoruacal solutions. The uptake or adsorption of copper, nickel and cobalt by finely divided oxide solids in aqueous ammoniacal medium has been investigated experimentally in order to determine how adsorption on leach residues can affect the recovery of leachable metals. Adsorption behavior was found to have maxima and minima as a function of pH, the magnitude of which depends on ammonia concentration, the metal cation, and the adsorbent. Osseo- Asare and D.W. Fuerstenav [15] developed Adsorption phenomena in hydrometallurgy 3 Model for coprq, nickel and cobalt uptake. The uptake of hydrolysable ions by oxide absorbents in aqueous ammoniacal solutions has been interpreted in terms of a mechanism involving the competitive adsorption of all the aqueous species. An adsorption model is presented which combines double layer theory with properties of the substrate (dielectric constant), the solvent medium (dielectric constant) and the aqueous ionic species (stability constants). Ning *et al.* [16] investigate effect of zinc and cerium addition on property of Copper based adsorbents for phosphine adsorption. A series of copper based activated carbon (AC) adsorbents were prepared in order to investigate the effect of Zn, Ce addition on Cu-based AC adsorbents for phosphine (PH_3) adsorption removal from yellow phosphorous tail gas. N_2 adsorption isotherm and X-ray diffraction (XRD) results suggested that the addition of Zn could increase the adsorbent ultra micropores, decrease the adsorbent supermicropores and the adsorbent average pore diameter. Therefore, it enhanced the PH_3 adsorption capacity. Appropriate amount of Ce addition could promote the reducibility of copper oxide, increase the thermal stability of adsorbent, and therefore enhance the PH_3 adsorption capacity. The present study indicated that the Cu-based adsorbents might be one of candidates for PH_3 removal from yellow phosphorous tail gas. Bose *et al.* [17] found that Critical evaluation of treatment strategies involving adsorption and Chelation for wastewater containing Copper, Zinc and Cyanide industrial wastewater containing heavy metals and cyanide requires treatment for removal of both metals and cyanide before disposal. Conventional methods for treatment of such wastewater involve alkaline – chlorination for cyanide destruction, followed for pH adjustment for metal precipitation, and subsequent removal of precipitate by solid-liquid separation processes. The objective of the study described in this paper is to critically evaluate treatment strategies involving some indigenous adsorbents and a low-cost chelating agent for treatment of a simulated wastewater. The evaluation procedure involved comparison of the performance of these treatment strategies with that of conventional treatment. Cheng Pan *et al.* [18] reported reusing sewage sludge ash as adsorbent for copper removal from wastewater. The sewage sludge ash (SSA) can potentially be used for removal of heavy metals from wastewater due to its similar chemical composition to that of fly ash and blast-furnace silage. The adsorption test of applying SSA into synthetic wastewater revealed that the adsorption isotherm of SSA for copper ions generally followed the Langmuir model. The primary mechanisms of copper removal by SSA included electrostatic attraction, surface complex formation, and cation exchange. Arias *et al.* [19] examined competitive adsorption and adsorption of copper and zinc in acid soils As an aid to evaluating the environmental threat posed by Cu and Zn when both are present in acid soils competitive and noncompetitive adsorption of Cu and Zn onto samples of the surface horizon of eight such soils was measured in batch experiments carried out at pH 5 with 0.01 M $NaNO_3$ as background electrolyte. The Langmuir−Freundlich equation was not appropriate for these data: it could not be fitted to the Zn data, and when fitted to the Cu data the uncertainty in the values of its parameters was too large for them to be useful. Desorption of Cu into $NaNO_3$ solution from previously Cu-loaded Soils in no case exceeded 11% of the Cu previously adsorbed, whereas analogous desorption of Zn was in all cases greater and ranged from 9% to 32%. Wayne Tuberville and Nora Yap [20] reviews the chemistry of Copper containing Sulphur adsorbents in the presences of mere tans. A brief review of the chemistry of copper and thiols is given, and a contrast is made to the behavior of copper-containing adsorbents used for the desulfurization of liquid hydrocarbon streams that are routinely treated in refinery processes. At a temperature of approximately 150^0C very well formed lamellar crystals of copper (I) thiolate are formed, which indicates that the copper migrates from the surface of the catalyst to expose bulk copper for further reaction.Turan *et al.* [21] worked Adsorption of copper and zinc tons on elite. Determination of the optimal conditions by the statistical design of experiments. In their study, a full factorial experimental design was utilized to access the effect of three factors on the adsorption of copper (II) and zinc (II) ions is an aqueous leachate of an industrial waste with little as adsorbent. The adsorption kinetics models, the second order model best described the data. Iolite was a reasonably effective adsorbent for Cu^{2+} and Zn^{2+} from aqueous leachates of industrial waste. Xiaomin Li *et al.* [22] produced Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. The preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co(II), Ni(II), Zn(II) and Cd(II) have been studied. Effects of different chemical modifications on the adsorbent properties including different alkalis saponification The maximum adsorption capacities of Ni(II), Co(II), Zn(II) and Cd(II) for SPA, SPA, SCA and SOA were obtained as 1.28, 1.23, 1.21 and 1.13 mol/kg and have increased by 95, 178, 60 and 130% The Langmuir and Freundlich adsorption isotherms models fitted the experimental data best with regression coefficient $R^2 > 0.95$ for all the metal ions. Elution efficiencies with different concentrations of HCl were evaluated. K. Poly chronopoulou *et al.* [23] utilized Novel Fe-Mn-Zn-Ti-O mixed metal oxides for the low temperature removal of H_2S from gas steams in the presence of H_2, CO_2 and H_2O.The efficiency of Fe–Mn–Zn–Ti–O mixed-metal oxides of varying composition prepared by sol–gel methods toward removal of H_2S from a gas mixture containing 0.06 vol% H_2S, 25 vol% H_2, 7.5 vol% CO_2, and 1–3 vol% H_2O was studied in the 25–100 °C range. In particular, a three times greater H_2S uptake at 25^0C compared with that on the commercial adsorbent was found. The work provides new fundamental knowledge that could trigger further research efforts toward the development of alternative mixed metal oxide not based on toxic. Qian et al. [24] characterized removal of Copper from aqueous solution using iron containing adsorbents derived from methane fermentation sludge. Iron- containing adsorbents prepared from methane fermentation sludge (MFS) were characterized by N2 adsorption, NRD, SEM, EDX, pH determination and elemental analysis. The results indicated that the adsorbent obtained at 7000C for 1 h in a steam atmosphere possessed the highest capability for Cu (II) adsorption. The Cu (II) adsorption onto the composite adsorbents in via ion-exchange with H, Ca and K ions, surface precipitation and binding with active sites on the surface of iron hydro oxides at various pH values. The adsorbents can be applied to remove copper from water or soil by fixation onto the surface.Runping Han et al. [25] evaluated characterization and properties of iron oxide coated zeolite as adsorbent for removal or copper (II) from solution in fixed bed column. A new composite adsorbent, iron, oxide coated zeolite (IOCZ), was characterized and employed for the removal of Cu (II) from aqueous solution using fixed bed column. The Thomas model was found suitable for the description of break through curve at all experimental conditions, while Adams- Bogart model was only for an initial part of dynamic behavior of the IOCZ column. The theoretical breakthrough curve was compared with experimental breakthrough curve profile in the dynamic process. Chen et al.[26] checked Preparation and Characterization of Pours granular ceramic containing dispersed aluminum and iron oxide as adsorbents for fluoride removal from aqueous solution. Porous granular ceramic adsorbents containing dispersed aluminum and iron oxides were synthesized by impregnating with salt solutions followed by precipitation at 6000C. Characterization studies on the adsorbent by SEM, XRD, EDS, and BET analysis were carried out to clarify the adsorption mechanism. The adsorbents were sphere in shape, 2-3 mm in particle size, highly porous and showed specific surface area of 50.69 sq m/g. The experimental data were well explained with pseudo- second- order kinetic model. Results from this study demonstrated potential utility of Al/Fe dispersed in porous granular ceramics that could be developed into a viable technology for fluoride removal from aqueous solution. Dellyanni et al.[27] analyzed Modelling the sorption of metal ions from aqueous solution by iron based adsorbents. The possibility of using iron-based adsorbents (i.e. akageneite or goethite) to remove heavy metal ions from aqueous solutions was the aim of the present review paper. Synthesized material was used in two forms, i.e. in fine powder of nanocrystals and in the form of grains (as granular). Typical adsorption models were discussed and the bed depth – service time equation has been applied to the sorption results in order to model the column operation. Wang et al. [28] discussed Micro wane – assisted preparation of bamboo charcoal-based iron – containing adsorbents for Cr (VI) removal. Bamboo charcoal – based, iron containing adsorbents (Fe-BC) was developed by using bamboo charcoal (BC) as a supporting medium for ferric iron that was impregnated by Fe2 (SO4)3 H2SO4 simultaneous treatment, followed by microwave heating. The results showed that the BET specific surface area, total pore volume. The adsorption of Cr (VI) onto Fe-BC was spontaneous and exothermic under the studied conditions. Column adsorption experiment with Fe-BC showed that Cr (VI) could be removed to below 0.05 mg/L within 360 bed volumes at empty bed contact time 2 min when the groundwater containing approximately 0.12 mg/L of Cr (VI) was treated. Tseng et al. [29] synthesized kinetics and equilibrium of adsorption removal of copper from magnetic polymer adsorbent. This study examined the desorption of copper ions, which were adsorbed on the magnetic polymer adsorbent (MPA) of polyvinyl acetate- aminoacidic acid (M-PVAC-IDA), by ethylenediamine interreacted acid (EDTA). Stage – wide desorption's were applied to remove the Cu(II) ions from the Cu (II) adsorbed M-PVAC-IDA (A-M-PVAC-IDA). Two simple kinetic models, the pseudo-first- order equation and pseudo- second – order equation, were employed to stimulate the kinetic behaviors of adsorption and desorption. The adsorption capacities (qe) estimated by the pseudo – first – order equation are more accurate in comparison with those simulated by the pseudo – second – order equation. The values of qi after CADOs are consistent with the predicted results via the previous work, evidencing that the adsorption behavior and the characteristics of the regenerated adsorbent of altered. Yiaomin Li et al. [30] prepared preparation and evaluation of orange peel cellulose adsorbents for effective removed or cadmium zinc, cobalt and nickel. The preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co (II), Ni(II), Zn (II) and Cd (II) have been studied. Effects of different chemical modifications on the adsorbed properties including different alkalis saponification (NaOH, NH4OH and Ca(OH)2) and different acids (C6H6O7H2O, H2C2O4, and H3PO4) modification after saponification with NaOH were investigated. Effects of initial pH, initial metal ions concentrations, shaking time and solid/ liquid ratio on metal ions biosorption were also investigated. Biosorption equilibriums were rapidly established in about 60 min and the adsorption kinetics model. It enhanced the PH3 adsorption capacity. Appropriate amount of Ce addition could promote the reducibility of copper oxide, increase the thermal stability of adsorbent, and therefore enhance the PH3 adsorption capacity. Ning et al. [31] showed Effect of zinc and cerium addition on property of copper-based adsorbents for phosphine adsorption. A series of copper –

based activated carbon (AC) adsorbents were prepared in order to investigate the effect of Zn, Ce addition on Cu-based AC adsorbents for phosphine (PH3) adsorption removal from yellow phosphorous tail gas. N2 adsorption isotherm and X-ray diffraction (XRD) results suggested that the addition of Zn could increase the adsorbents ultrararer, decrease the adsorbent supermicropores and the adsorbents average pore diameter. S. Vellaichamy and K. Palanivelu [32] was carried out Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid phase extraction on to MWCNTS impregnated with D2EHPA- Topo mixture A solid phase extraction method has been developed for the determination of copper, nickel and zinc ions in natural water samples. This method is based on the adsorption of copper, nickel and zinc on multiwalled carbon nanotubes (MWCNTs) impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO). The developed method was applied for the determination of copper, nickel and zinc in electroplating wastewater and real water sample with satisfactory results (R.S.D.'s <10%).Allah M. Deraz [33] studied Catalytic oxidation of carbon monoxide on non-doped and zinc oxide doped nickel alumina catalyst Alumina-supported NiO catalysts, promoted with 0.14–3 wt.% ZnO, were 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 maximum increase in the catalytic reaction rate constant per unit surface area measured at 250 °C ($\overline{k}_{250\ °C}$) due to doping with 3 wt.% ZnO attained 78 and 217% for the catalysts calcined at 400 and 600 °C for 4 h, respectively. Beigin Bayat [34] discovered Comparative study of adsorption properties of Turkish fly ashes 1. The case of nickel (ii), copper (ii) and zinc (ii). The objective of this study was to compare two different Turkish fly ashes (Afsin-Elbistan and Seyitomer) for their ability to remove nickel [Ni(II)], copper [Cu(II)] and zinc [Zn(II)] from an aqueous solution. The effect of contact time, pH, initial metal concentration and fly ash origin on the adsorption process at 20±2 °C were studied. The effectiveness of fly ash as an adsorbent improved with increasing calcium (CaO) content. Adsorption data in the range of pH values (3.0–8.0) using Ni(II) and Cu(II) concentrations of 25±2 mg/l and Zn(II) concentration of 30±2 mg/l in solution were correlated using the linear forms of the Langmuir and Freundlich equations. Han et al. [35] developed Characterization and properties of iron oxide coated zeolite as adsorbents for removal of copper (II) from solution in fixed bed column. A new composite adsorbent, iron oxide coated zeolite (IOCZ), was characterized and employed for the removal of Cu (II) from aqueous solution using fixed bed column. The effects of various experimental conditions, such as the flow rate, initial metal concentration and bed depth, were studied. The dynamics of the adsorption process were fitted by Adams – Bohart model and Thomas model. The bed depth service time (BDST) model was applied to predict the service times with other flow rate and initial concentration.

CONCLUSION:

Above mentioned literature shows wide applications of metal /mixed metal oxides as adsorbent in various reactions like preparation and evaluation of orange peel cellulose adsorbents for effective removed or cadmium zinc, cobalt and nickel. The preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co (II), Ni (II), Zn (II) and Cd (II) have been studied. Effects of different chemical modifications on the adsorbed properties including different alkalis saponification (NaOH, NH4OH and Ca (OH)2) and different acids (C6H6O7H2O, H2C2O4, and H3PO4) modification after saponification with NaOH were investigated. Effects of initial pH, initial metal ions concentrations, shaking time and solid/ liquid ratio on metal ions biosorption were also investigated. So, metal/mixed metal oxides have broad applications as adsorbent in various chemical reactions.

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