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Synthesis, characterization and catalytic studies by zeolite encapsulated hexaazamacrocyclic complexes of nickel(II) and copper(II)

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ABSTRACT

The nickel(II) and copper(II) complexes of the 16-membered 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}] octadecane (THA) were synthesized by in situ one-pot template method. The nickel(II)THA and copper(II) THA complexes are represented as NTHA and CTHA respectively. The encapsulation of free complexes (FC) (*i.e.* NTHA and CTHA) in the cavities of zeolite-Y was achieved by ship-in-bottle method. The zeolite encapsulated metal complexes (ZEMC) are represented as NTHAY and CTHAY. The retention of the free complex with ZEMC was investigated by spectral, thermal, sorption and microscopic techniques (*i.e.*, FTIR, ESI-mass, DRS/UV–visible, XPS, TGA, XRD, nitrogen adsorption isotherm, SEM and TEM). The NTHA, CTHA, NTHAY and CTHAY were employed as catalysts for the oxidation of Reactive Red 198 (RR) and Phenol Red (PR) dyes under UV irradiation. The ZEMC exhibits higher catalytic activity for the degradation of dyes, when compared to that of FC. The reusable photocatalysts show comparable activity to that of the fresh catalysts.

1. Introduction

Transition metal complexes play an important role in the field of catalysis and photocatalysis [1,2]. The recovery of transition metal complexes from the products in homogeneous medium is a challenging task. In order to overcome this problem, the heterogenization of homogeneous catalyst was adopted [3,4]. However, the enhancement of catalytic activity with nickel(II) and copper(II) based composites is alternative to highly expensive metals such as ruthenium, rhodium and platinum [5]. Hence, impregnation of homogeneous transition metal complexes into a solid support, such as polymer, zeolite and MCM41, was attempted [6]. Zeolites are made up of aluminosilicates known as “solid acid” and are better substitutes to commercially available toxic chemicals such as sulphuric acid, potassium dichromate and phosgene [7]. The zeolites are good low cost exchange molecular devices for transition metal ions due to their intra crystalline cavities. The aluminosilicates are models for the NaY- zeolite in which the M^{2+} ions ($M^{+2} = Ni^{+2}$, Cu^{+2}, Co^{+2}, Zn^{+2} and Ru^{+2}) were exchanged with Na^{+} ions present within the tetrahedral aluminosilicate units. These ion-exchanged M^{2+} ions are homogeneously distributed throughout the pores of $(Si/Al)O_4$ units [8,9]. They are potential building blocks and act as photocatalysts for the destruction of synthetic organic dye molecules. The surface water contains toxic colorants such as organic dyes, phenolic compounds and other inorganic metal ions, which cause environmental problems [10–12]. Hence, the active surface materials exhibit many advantages in photocatalytic degradation process and they can act as adsorbents and degrade the synthetic dye molecules. These materials posses potential advantages over other methods such as the use of organic block polymer chains [13,14]. The oxidation reaction of dye removal of the impregnated metal complex with silica frame work can result in good catalytic activity and selectivity, when compared to structurally disordered complexes [15].

The copper, cobalt and nickel-salicylaldehyde phenylhydrazone (SAPH) complexes encapsulated in zeolite matrix were used as photocatalysts in the removal of Acid Violet 1. The zeolite encapsulated Cu(II) complex exhibits higher catalytic efficiency when compared to those of Ni(II) and Co(II) [16]. The sulfated Mo-doped TiO_2@fumed SiO_2 composite exhibits good photocatalytic activity under both ultraviolet and visible light irradiation against methyl orange degradation [17]. The zeolite-Y impregnated Ruthenium(II)-tris-bipyridine/titanium dioxide ($Ru(bpy)_3^{2+}/TiO_2/Y$) are used as

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efficient heterogeneous photocatalysts in solar Fenton-type oxidation reactions [18]. The complex Fe(III)-[2-(hydroxybenzylidene)-amino]benzoic acid (Fe(III)-L/Aen) has been encapsulated in pores of zeolite. The resulting host/guest compound including H_2O_2/UV is active system for the oxidative color removal of Direct Blue 1 in aqueous heterogeneous suspensions with very low catalyst/substrate ratio. The heterogenized complex especially Fe(III)-L/Aen is significantly more stable than the corresponding homogeneous complex over prolonged reaction time, and therefore a better catalyst than the homogeneous complex [19]. The synthesis of the hexaazamacrotricylic complexes in the cavity of zeolite by ship-in-bottle method and their application in the degradation of dyes are yet to be reported. Hence, the photo degradation of dyes by supported hexaazamacrotricylic complexes under UV and visible light source has been investigated.

In the present investigation, the synthesis of the nickel(II) and copper(II) complexes with 16-membered hexaazamacrotricyclic ligand by template method is described. These complexes are effectively impregnated in the cavities of zeolite-Y. The reported catalytic efficiency was checked towards the removal of Reactive Red 198 (RR) and Phenol Red (PR) under UV irradiation. The activities of the ZEMC along with the FC are determined by spectrophotometric techniques.

2. Experimental

2.1. Materials

Diethylenetriamine, formaldehyde (Loba Chemie. Pvt. Ltd., India), nickel carbonate, copper carbonate, Phenol Red (Fisher Scientific, India), Zeolite-Y (Sigma-Aldrich, India) and Reactive Red 198 (Textile industry, Tamilnadu) were used without further purification. Millipore water was used throughout the work.

2.2. Physicochemical measurements and characterization

Infrared spectra of the free and grafted complexes were recorded in the region 400 to 4000 cm^{-1} by using KBr pellets on a Perkin-Elmer 8300 FTIR spectrometer. DRS/UV–visible spectrum is a very effective technique for getting information about d-d transitions and charge transfer transitions in metal complexes encapsulated in solid support from which, coordination geometries of the encapsulated complexes can be obtained. Diffuse reflectance spectra of the zeolite encapsulated metal complexes (ZEMC) were recorded at room temperature in the wavelength range of 200–800 nm on a Perkin-Elmer lambda 650 double beam spectrophotometer. The UV–visible spectra of liquid samples were recorded on a Perkin-Elmer Lambda-35 spectrophotometer. The X-ray Photoelectron Spectroscopic (XPS) surface speciation analyses of the compounds were carried out by Omicron nanotechnology, ESCA-14. 1000XM-Monochromator, Al Kα radiation with 1486.7 eV. The instrument was operated at 300 W. The compounds were made as pellets and used for XPS analysis. The XPS peak data were calibrated to C1s core peak. The crystalline nature of all compounds were studied by powder X-ray diffraction using Bruker D8 Advance X-ray diffractometer with monochromatic Cu-Kα_1 radiation ($\lambda = 1.5418$ Å). The sample was recorded over the diffraction angle (2θ) range between 1° and 70°. In the thermo gravimetric analysis (TGA), the samples to be analysed are subjected to a controlled heating to high temperature at a specified heating rate of 278 K/min. TGA experiments were performed with Versa Therm Cahn thermo balance TG-151 with a sensitivity of 10 μg attached to an analytical thermal system in the atmospheric pressure. The experiments were conducted in the temperature range of 300–1173 K. The N_2 adsorption and desorption isotherms and Brunauer–Emmett–Teller (BET) specific surface area measurements were carried out at 77 K on a Micrometrics ASAP (Model 2020) surface area analyzer using nitrogen and helium gases with a purity of 99.999%. The analyzer is equipped with two independent vacuum systems, one for sample preparation and the other for sample analysis. In the first step, the sample tube containing solid materials was evacuated to 50 μm Hg for two hours at 373 K. Most of the computational procedures in current use are related to the BJH method, proposed by Barrett, Joyner, and Halenda. These procedures are based on the notional emptying of the pores by a stepwise reduction of P/P_0, allowance being made for the thinning of multilayer in those pores already emptied of condensate. The derived meso/micro pore size distribution is usually expressed in the graphical form pore size (Å) versus pore volume (cm^3/g) which reveals the porosity volume distribution in terms of cubic centimetres over the pore size range of 20–50 Å. Field Emission Scanning Electron Microscopy (FESEM) Surface morphology of solid state catalysts was investigated using a HITACHI-S3890 Scanning Electron Microscope (SEM), the powder sample was directly used for the analysis. The morphological analysis was carried out by a FEI TECNAI G2 (T-30) High Resolution Transmission Electron Microscope (HRTEM) with an accelerating voltage of 250 kV. After dispersing the sample in water by bath sonication, the sample specimens are coated equally on the copper grid for the TEM analysis.

2.3. Synthesis of NTHA macrocyclic complex

Nickel(II) complex of the 16-membered 1,3,6,9,11,14-hexaazatricyclo[$12.2.1.1^{6,9}$] octadecane (NTHA) was synthesized by the one-pot template method. The nickel acetate (3.9 mmol, 0.9 g) was stirred in 50 mL anhydrous methanol and then diethylenetriamine (7.8 mmol, 0.84 mL) and 36% formaldehyde (0.016 M, 0.47 mL) were added to the stirred solution. The reaction mixture was heated at reflux for 3 h. An excess of sodium perchlorate (15.6 mmol, 1.8 g) was added to the reaction mixture and the solution was stirred at room temperature until yellow precipitate was formed. The product was filtered out, washed with methanol, diethyl ether and recrystallized from water, Yield 1.65 g (80%) [20].

2.4. Synthesis of CTHA macrocyclic complex

Copper(II) complex of the 16-membered 1,3,6,9,11,14-hexaazatricyclo[12.2.1.16,9] octadecane (CTHA) was synthesized by one-pot template method. The copper acetate (3.5 mmol, 0.7 g) was stirred in 50 mL anhydrous methanol and then diethylenetriamine (7.1 mmol, 0.82) and 36% formaldehyde (0.014 M, 0.42 mL) were added to the stirred solution. The reaction mixture was heated at reflux for 6 h. An excess of sodium perchlorate(14 mmol, 1.7 g) was added to the reaction mixture and the solution was stirred at room temperature until blue precipitate was formed. The product was filtered out, washed with methanol, diethyl ether and recrystallized from water. Yield 1.1 g (65%). The MTHA complexes are soluble in water, acetone, acetonitrile and DMSO but insoluble in alcohol. The trans type hexaazamacrotricyclic complexes i. e Ni(II)THA.2ClO_4 & Cu(II)THA.2ClO_4 are represented in Scheme 1 [20].

2.5. Synthesis of the bis(deta)M(II)-Y

The precursor complex in methanol was synthesized from stoichiometric amounts of diethylenetriamine and with the corresponding metal perchlorates. A solution containing 0.01 M of M(II) ClO_4 and 0.02 M diethylenetriamine at room temperature was added separately and the stirring was continued for 12 h. The product was isolated on cooling the reaction mixture and the