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Oxidative Treatment of Rhodamine B Solution on CoO_x /sepiolite Catalysts

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Abstract: Sepiolite loaded with different cobalt oxide contents has been prepared by the precipitation method followed by calcination at 410°C. The synthesized Co-loaded samples were characterized by physical methods using XRD, SEM, BET, and H₂-TPR. The obtained solids have a large specific area and good distribution of cobalt oxide nanoparticles on sepiolite carrier. The catalysts were tested for the oxidative removal of rhodamine B solution and found that 1.0-3.0 wt.% cobalt ion/sepiolite samples exhibited the highest decoloration efficiency of rhodamine B (88-90%) in the presence of hydrogen peroxide at room temperature after the treatment of 30 mg/L of RhB solution in 210 minutes.

Keywords: Sepiolite, CoO_x , Rhodamine B, Degradation, Advanced Oxidation

1. Introduction

Nowadays, effluents from textile dyeing industry have caused water colored pollution and affected strongly on human life. According to recent statistics, 800,000 tons of organic dyes such as rhodamine B (RhB), crystal violet, methylene blue, Congo red, indigo dye, and methyl orange are annually produced^[1,2]. The residues of such dyes in industrial waste water always are a big challenge for environmentalists and scientific community as well. Indeed, the colored water has threatened directly to the water resource and aquatic life. Therefore, the demand for the treatment of organic dyes dissolved in water has been heavily pressurized for the last decade^[2,3]. Traditionally, several physical and chemical treatments have been developed for the effective treatment of color compounds in waste water^[2,4-6]. Nevertheless, these conventional methods have faced some environmental challenges and usually require the post-treatment in order to remove efficiently color compounds in water^[5,7-9]. For example, a large amount of sludge disposal was created during the chemical and physical treatments^[7,8-10-12]. Especially, adsorption, filtration processes did not destroy organic dyes which only incorporated them into the sludge waste^[8,11,12]. On the contrary, advanced oxidation processes for the destruction of organic compounds have aroused much attractive in recent years^[5,12-16]. Particularly, heterogeneous catalysts are of great interest for chemically advanced treatment of waste water because of their abilities to undergo the selective oxidation process to produce less hazardous products. In metal oxide supported-catalysts, transition metals in group VIIB always are potential candidates for the oxidation-reduction catalyst system^[3,5,7,12,17]. The catalytic activity of these metal oxides may improve remarkably if they are dispersed on a porous support. In this way, cobalt oxide particles are loaded on sepiolite and used as heterogeneous catalysts for the degradation of rhodamine B aqueous solution.

The purpose of this work is to disperse CoO_x nanoparticles on sepiolite matrix to prepare a set of effective catalysts for the oxidative removal of RhB in water. The reason of using sepiolite as a carrier is due to its particular structure. Indeed, the hydrated magnesium silicate has the formula $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ (two sheets of SiO_4 tetrahedral and a sheet of MgO octahedral) with fibrous structure and open channel network^[6,17-20]. The opening structure of sepiolite would control the particle size of cobalt hydroxides and stabilize active sites of CoO_x on the external surface. It is therefore expected that CoO_x /sepiolite would be an excellent catalyst candidate for the oxidative removal of rhodamine B.

2. Experimental

2.1 Catalyst preparation

3.0 grams of sepiolite (Sigma-Aldrich) was put into a 250 mL-flask containing 100 mL of cobalt nitrate salt (Sigma-

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Aldrich, $\geq 98\%$) solution and then an excess of sodium hydroxide (Sigma-Aldrich, $\geq 98\%$) solution (0.05M) was dropped in the suspension until pH = 8.5. The suspension was kept for 2 h under magnetic agitation. The resultant was filtered, washed with warm distilled water several times until pH = 7, and then dried at 75 oC for 24 h in oven. After that the filter cake was calcined at 410oC for 4 h. The obtained catalysts are designated as x% Co/Sep in which x is the weight percentage of cobalt ions on the sepiolite.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected on a D8 Advance-Bruker apparatus CuK α radiation (λ = 1.54059 Å). Fourier transform infrared (FT-IR) spectra were run in 4000-400 cm $^{-1}$ window on a DX-Perkin Elmer spectrometer (USA). The scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 (Japan). TEM micrographs were recorded on a Japan JeolJEM-1010. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. 200-300 mg of each sample was degassed at 150oC for 5h in to eliminate the humidity prior to nitrogen adsorption experiments. Temperature programmed reduction of hydrogen (H $_2$ -TPR) measurement in the range of 293-1073K was done on Gow-Mac 69-350 with thermal conductivity detector. The heat rate is 10°C/min.

2.3 Degradation of rhodamine B aqueous solution

0.10 grams of powdered catalyst was added in 100 mL RhB (Sigma-Aldrich, 95%) aqueous solution under magnetically stirring at room temperature (28°C). A given volume of hydrogen peroxide H $_2$ O $_2$ (35 wt.%) solution was added at once. 5 mL of reaction solution was withdrawn at given time intervals for the measurement of rhodamine B (RhB) concentration. The degradation efficiency (%) is defined as equation (1):

$$\text{Degradation Efficiency (\%)} = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

where C $_0$ and C $_t$ are the initial concentration and the measured concentration of rhodamine B at a given time (t), respectively. The degradation efficiency of RhB was calculated using UV-vis spectra by measuring a maximum absorbance of RhB at wavelength of 553 nm (Shimadzu, Cary 100 UV-Vis spectrophotometer).

3. Results and Discussion

3.1 Catalyst characterization

Phase structure of all prepared solids was determined by X-ray diffraction technique. Figure 1 indicates that sepiolite structure is still preserved for cobalt oxide-loaded magnesium silicate solids, reflecting by the appearance of some diffraction peaks at 2-theta of 7.54, 20.89, 35.29° in XRD diffractodiagram (JCPDS No. 01-075-1597).

Figure 1. Powder-XRD patterns of CoO $_x$ /sepiolite samples

It is observed no clear reflection signals for cobalt oxides at low loading content samples, possibly due to a very high dispersion of CoO $_x$ tiny species on the support. For a higher CoO $_x$ loading sample (7% Co/sepiolite) XRD spectrum shows a weak diffraction line at 2-theta of 36.8o which is indexed for (311) plan of Co $_3$ O $_4$ crystallites (JCPDS No. 01-074-1657)^[17].

^{19, 20-23]}. The presence of Co_3O_4 was also confirmed by FT-IR analysis. As shown in Fig. 2, FT-IR spectra of $\text{CoO}_x/\text{sepiolite}$ shows a visible shoulder at 665 cm^{-1} which is essentially assigned to the vibration of Co-O bonds of CoO_x ^[20]. The other bands belong to the O-H vibration modes. The broad band at 3420 cm^{-1} is solely attributed to O-H stretching mode for hydroxyl groups on the surface. The weaker peak at 1650 cm^{-1} is typically ascribed to the O-H bending mode of adsorbed water molecules. The lattice vibrations of the sepiolite were characterized by a weak band at 1215 cm^{-1} related to the Si-O stretching modes and the one at 1015 cm^{-1} ascribed to the Si-O-Si plan vibration. A band at 690 cm^{-1} is ascribed to the Mg_3OH -bending vibration and the other at 475 cm^{-1} is attributed to the Si-O-Mg of the octahedral-tetrahedral linkage^[19, 20, 24].

Figure 2. FT-IR spectra of $\text{CoO}_x/\text{sepiolite}$ samples

Scanning Electron Microscopy (SEM) was used to identify the morphological characteristics of sepiolite and $\text{CoO}_x/\text{sepiolite}$. Figure 3a and 3b shows a handful of nanofibers of hydrated magnesium silicates. These fibers are likely oriented in one direction. In some parts, they are closely packed together. An observable difference in morphology between sepiolite and $\text{CoO}_x/\text{sepiolite}$ was shown in Fig. 3a and 3b. The surface of 5%Co/sepiolite is rougher than sepiolite due to the deposition of CoO_x species on the sepiolite nanofibers. The diameter of these fibers is about of 50-60 nm as indicated by TEM images (Figs. 3c and 3d). However, both SEM and TEM images indicate large empty volumes magnesium silicate among bundles. The external surface area of these solids is rather high.

Figure 3. SEM micrographs (a, b) and TEM (c, d) images of sepiolite and 5% Co/sepiolite

The specific surface area of sepiolite and CoO_x /sepiolite catalysts was measured by nitrogen adsorption/desorption method. Figure 4 depicts isothermal adsorption/desorption profiles of sepiolite and CoO_x -loaded samples. The profile shape of the prepared solids is close to the type IV according to the IUPAC classification. In addition, the adsorption and desorption curves likely superimposes together in the relative pressure range of 0 - 0.8, characterizing for the microporous materials. Moreover, desorption line separates from the adsorption curve in the range of 0.8 - 1.0, giving in a narrow hysteresis loop. This loop falls into the type H_3 definition, which is firmly attributed to condensation of nitrogen molecules in some slit-shaped mesopores in the solids^[4, 12, 13, 17-19].

As a result, the specific area of prepared catalysts increases with increasing amount of cobalt oxide in the samples (Fig. 4), possibly resulted from the precipitation of cobalt ions in basic environment accompanied by washing and calcinating steps^[17, 19]. Under basic media of cobalt hydroxide - sepiolite suspension, silicate and other oxide impurities were removed after washing steps. Thus, channels and tunnels of the support become clearer. Another reason is that the deposition of CoO_x particles on the sepiolite creates more empty spaces between nanorods due to the less ordered arrangement, in good harmony with microscopic results in Fig. 3. Therefore, it is indicated that this preparation procedure has some positive effects on the external surface area of samples, leading to an increased specific area on higher loading CoO_x samples.

Figure 4. Nitrogen adsorption-desorption isothermal profiles of sepiolite and Co/sepiolite samples

Figure 5. H_2 -TPR results of Co/sepiolite samples

Since XRD results demonstrated the presence of cobalt oxides on sepiolite only, H_2 -TPR experiment was used to investigate the nature of cobalt oxide phases in catalysts. Figure 5 shows two broad peaks in H_2 -TPR profiles of CoO_x /sepiolite samples, implying the occurrence of the reduction of cobalt oxides in consecutive stages. This is supported by XRD result which corroborates the existence of a multiple-phase of cobalt oxides in the catalyst. As a consequence, the broad peak at 259 °C is assigned for the reduction of Co_3O_4 to CoO while the one at 436 °C was due to the reduction of CoO to metallic cobalt, in good agreement with the data reported in the literature^[13, 17, 20-23]. Furthermore, the reduction peaks are rather broad, inferring the cobalt oxide particles stayed on different environmental conditions. In practice, cobalt oxide particles particularly located on the edge of sepiolite nanorods are reduced at a lower temperature. The reduction temperature shifts slightly to right if the cobalt species are distributed in the sepiolite channels or tunnels^[13, 17]. Thus, the location of CoO_x species may effect on the catalytic activity of CoO_x /sepiolite in the degradation of rhodamine B in water^[17, 20, 21]. The baseline of H_2 -TPR profile gradually increases at higher temperatures due to the changes in the sepiolite structure^[17-19].

3.2 Oxidative removal of rhodamine B aqueous solution

The catalytic oxidation of rhodamine B dye in water has been carried out using H_2O_2 aqueous solution at room temperature (28 °C) and atmospheric pressure. Observable changes in the concentration of rhodamine B were withdrawn from the variation in maximal absorption in a UV-vis spectrophotometer at 553 nm.

3.2.1 Effect of cobalt oxide content

A set of rhodamine B decolorization experiments was carried out in the same reaction conditions in addition a blank test (no catalyst). As expected, the blank experiment shows very low degradation efficiency while sepiolite can remove about 52-53% of rhodamine B. When sepiolite carries cobalt ions, the degradation efficiency of RhB significantly improves from 52% on sepiolite parent to 88-90% on CoO_x /support catalysts. In more detail, Figure 6 indicates that the degradation efficiency of RhB increases sharply during the first 30 min and then gradually approaches a maximum value of RhB decomposition after 180 min.

A similar variation of removal rhodamine B during the beginning time between sepiolite and CoO_x -containing catalysts demonstrates the occurrence of physical and chemical changes in 30 min. A higher degradation efficiency is observed on CoO_x /sepiolite catalysts demonstrating the catalytic role of cobalt ions in the oxidation of rhodamine B. Under present conditions, cobalt(II) ions on the sepiolite channels serve as active sites the decomposition of H_2O_2 to form $\text{HO}\cdot$ radicals which are highly active species attacking rhodamine B molecules^[17, 20, 24-27]. Therefore, the degradation efficiency of RhB is also dependent on the amount of cobalt oxide loadings. The activity of catalysts decreases in the order of 3%Co/Sep > 1%Co/Sep > 5%Co/Sep > 7%Co/Sep (Fig. 6).

Figure 6. Effect of cobalt ion content loaded on sepiolite on the degradation efficiency of RhB (30 mg/L of rhodamine B, 0.10 g of catalyst, 1.0 mL of H_2O_2 , room temperature)

Figure 7. UV-vis absorption spectra of rhodamine B aqueous solution in CoO_x /sepiolite catalysts after 210 min (a) and UV-vis absorption spectra of rhodamine B aqueous solution over 3%Co/sepiolite catalyst (b) (30 mg/L of rhodamine B, 0.10 g of catalyst, 1.0 mL of H_2O_2 , room temperature)

Analysis of activity series of CoO_x /sepiolite brings us important information of catalytic behavior of CoO_x /sepiolite in the oxidative removal of rhodamine B. Indeed, the catalytic activity is related to the dispersion of CoO_x on support and density of catalyst in the suspension. Increasing cobalt ion content from 1.0 to 3.0% provides more active components

in the reaction mixture. A small amount of CoO_x is highly dispersed on the hydrated magnesium silicate nanofibers. A lower degradation efficiency of RhB on 5.0 – 7.0%Co/sepiolite is due to the agglomeration of cobalt oxide particles in the catalyst. This explains similar degradation efficiency values between 7% Co/sepiolite sample and the parent support (Fig. 6).

To investigate the elimination ability of rhodamine B on catalysts, we have monitored the UV-vis spectra of rhodamine B aqueous solution during the reaction. Figure 7a displays UV-vis spectra of RhB in solution after 210 min. It is observed only a reduction of absorbance at wavelength of 553 nm. No observable shift in absorbance wavelength was observed, reflecting the chromophore cleavage of rhodamine B caused by hydroxylation and aromatic opening^[12, 24-27]. Meanwhile, Figure 7b reports the UV-vis absorption spectra of the dye solution versus reaction time. Similar to what is observed in Fig. 7a, the absorbance at 553 nm gradually reduces intensity along with increasing the treatment time, reconfirming that the chromophores conjugated π -system was destructed under reported experimental conditions. In addition, no new peak was detected between 300 and 600 nm (Fig. 7) because the intermediates resulted from destruction of RhB molecules have no conjugated π -systems^[12, 16, 24, 25, 28-30].

3.2.2 Effect of oxidant amounts

As seen in Figure 6, H_2O_2 oxidant has great ability to oxidize rhodamine B aqueous solution over CoO_x /sepiolite catalysts. An amount of H_2O_2 in the reaction system is also an important parameter for the degradation, thus a set of experiments was performed the oxidation of 30 mg/L of RhB with different volumes of H_2O_2 solution and experimental data are represented in Fig. 8. In this case, about 50% of RhB was physically adsorbed on the catalyst if no H_2O_2 oxidant was added into the reaction system. This result is equivalent to the experimental data obtained from the experiment done on sepiolite (dashed line in Fig. 6). Secondly, the degradation level of rhodamine B increases from 50 to 90%, as more amount of H_2O_2 was added to the reaction mixture^[19, 22, 23]. When 0.5 mL of hydrogen peroxide solution was dropped into the reaction solution, the maximum degradation efficiency of RhB was about 78% because H_2O_2 is the limiting agent in this experiment.

An increased amount of H_2O_2 leads to increasing degradation efficiency, but the conversion of RhB likely reaches plateau after 150 min-on-time. Indeed, the destruction of RhB chromophores depends on the concentration of $\text{HO}\cdot$ radicals dissociated from H_2O_2 . Thus, the reaction rate of RhB decomposition is essentially rational to the amount of H_2O_2 added^[22, 27, 28, 30, 31]. Therefore, next experiment series investigate the effects of catalyst dose on the removal of RhB in water.

Figure 8. Effect of H_2O_2 amounts on the degradation efficiency of RhB on 3%Co/sepiolite catalyst (30 mg/L of rhodamine B, 0.10 g of catalyst, room temperature)

3.2.3 Effect of catalyst dose

Another factor contributing to the removal efficiency of rhodamine B is the quantity of catalyst added to organic dye solution. In this section, a series of tests with catalyst dosages is reported in Fig. 9. In line with Figure 6, the degradation efficiency of RhB is proportional with the amount of active sites^[25, 27-31].

Figure 9. Effect of catalyst mass on the degradation efficiency of RhB on 3%Co/sepiolite catalyst (30 mg/L of RhB, 0.10 g of catalyst, 1.0 mL of H_2O_2 , room temperature)

Therefore, more amount of catalyst is added to the reaction mixture, higher degradation efficiency of RhB is in the range of 0 - 0.15 mg/L as observed in Fig. 9. The highest decolorization degree was observed in the experiment having 0.15 - 0.2 g of catalyst. Figure 9 also reveals no remarkable difference in degradation efficiency of RhB is observed in the experiment of 0.15 and 0.20 gram of catalysts used after 150 min. As a result, a higher dosage of catalysts would not affect the oxidation ability of rhodamine B with H_2O_2 .

3.2.4 Effect of rhodamine B concentration

Figure 10. Effect of rhodamine B concentration on the degradation efficiency over 3%Co/sepiolite catalyst (30 mg/L of RhB, 0.10 g of catalyst, 1.0 mL H_2O_2 , and room temperature)

Because a remarkable amount of RhB physically adsorbed on the porous support of the catalyst, the changes in initial concentration of RhB were performed to study the oxidative behavior of the catalysts^[3, 12, 16, 24]. Figure 10 exhibits all degradation efficiency plots versus reaction time in the experiments using 20 -70 mg/L of RhB solution. It is noted here that H_2O_2 amount is fixed in the system, an increased concentration of RhB results in decreasing the degradation efficiency of RhB. In practice, the degradation efficiency of RhB declines from 93 to 62% as RhB initial concentration rises from 20 to 70 mg/L. This is interpreted by the fact that an excess of rhodamine B condition, the amount of $HO\cdot$ radicals in the reaction mixture would only attack a small amount of dye molecules^[25, 28, 32, 33]. An existence of unreacted molecules of RhB in the reaction mixture gives rise to decrease the degradation efficiency^[32, 31-34]. Furthermore, the sample of 5%Co/Sep has recycled catalysts three times with no significant changes in chemical decolorization of 30 mg/L of rhodamine B.

In the case of sample 3%Co/Sep, two-cycling tests were performed with 30 mg/L of RhB and no measurable changes in degradation efficiency were observed.

4. Conclusions

The deposition of cobalt(II) ions on the hydrated magnesium silicate nanofibers leads to the formation of CoO_x -highly dispersed sepiolite catalysts with $x = 1$ and 1.5 . CoO_x nanoparticles are distributed in the open channel network and on the edge of sepiolite fibers. The total specific surface area of the prepared catalysts increases with CoO_x loadings. All CoO_x /sepiolite were used as catalysts for the oxidative reaction of rhodamine B aqueous solution. The catalyst exhibited both adsorbability and catalytic oxidation of RhB with H_2O_2 . CoO_x species play as active component for the destruction of RhB to form the intermediates without π -conjugated systems. The degradation efficiency of RhB depends strongly on reaction conditions such as H_2O_2 amount, catalyst dosage, rhodamine B concentration. The highest degradation efficiency of RhB was obtained on 1.0 – 3.0 wt.% Co/sepiolite samples with 88-90% at mild conditions. Our findings indicate that CoO_x -loaded sepiolite catalysts are rather effective catalysts for the degradation of rhodamine B in water.

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