THE INFLUENCE OF SODIUM HYDROXIDE CONCENTRATION ON THE PHASE, MORPHOLOGY AND AGGLOMERATION OF COBALT OXIDE NANOPARTICLES AND APPLICATION AS FENTON CATALYST

E. L. VILJOEN[a,*], P. M. THABEDE[a], M. J. MOLOTO[a], K. P. MUBIAYI[b],
B. W. DIKIZA[a]
[a]Department of Chemistry, Vaal University of Technology Private, Bag X021, Vanderbijlpark 1900, South Africa
[b]School of Chemistry, University of the Witwatersrand, 1 Jan Smuts Avenue, Braamfontein Johannesburg 2000, South Africa

The concentration of NaOH was varied from 0.2 M to 0.7 M during the preparation of the cobalt oxide/cobalt oxide hydroxide nanoparticles by precipitation and air oxidation. Cubic shaped and less well defined Co_3O_4 nanoparticles formed at 0.2 M NaOH. An increase in the NaOH concentration increased the number of well-defined cubic shaped nanoparticles. Agglomerated CoO(OH) particles with different shapes formed at the highest NaOH concentration. The cubic shaped Co_3O_4 nanoparticles were subsequently used as catalyst for the Fenton degradation of methylene blue and it was found that the least agglomerated nanoparticles were the most catalytically active.

1. Introduction

Controlling the size and the shape of nanoparticles using simple, inexpensive precipitation methods without sophisticated capping molecules, remains a challenge. Literature has indicated that the concentration of the base (pH) is an important parameter to control the size, shape and phase of metal oxide nanoparticles. Obodo et al.[1] used chemical bath deposition at atmospheric pressure and 70 °C to precipitate Co_3O_4 crystallites on a glass substrate and they showed that the crystallite sizes were larger at a higher pH of 12 in comparison to when a pH of 10 was used. In contrast, Nugroho and Kim [2] found a decrease in the crystallite size and a change in phase from Co_3O_4 to CoO with an increase in the concentration of KOH (0.0 M to 0.5 M) used under supercritical water conditions of 400 °C and 30 MPa. Li et al. [3] used a low reaction temperature of 90 °C and showed that with an increase of NaOH concentration from 3 M to 5 M the shape changed from a mixture of nanoparticles and nanoplates to irregular shaped nanoplates. Feng et al.[4] prepared Co_3O_4 using a hydrothermal method at 160 °C and by increasing the cobalt acetate to NaOH ratio from 1:0.75 to 1:2, the shape changed from imperfect cubes consisting of small particles, to well defined cubes and finally to hexagonal particles. Similarly, Kanie et al. [5] determined that cubic shaped particles changed to hexagonal shaped particles when the pH was increased above 8 at a reaction temperature of 250 °C. The manner in which the concentration of the base (pH) affects the morphology of the cobalt oxide nanoparticles seems to depend on the particular method used since no clear trend could be extracted from literature.

Previously we have found that the acetate ion plays an important role in obtaining cubic shaped Co_3O_4 nanoparticles and cobalt acetate was thus chosen as cobalt source [6]. In this study the effect of NaOH concentration was investigated with the aim to develop a method to prepare non-agglomerated, well defined cubic nanoparticles at atmospheric pressure and temperatures below 100 °C.

The Fenton oxidation reaction can be used to remediate water polluted by organic molecules that are recalcitrant to degradation. Methylene blue dye is an example of such an

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* Corresponding author: elverav@vut.ac.za

organic pollutant. The Fenton reaction is catalysed by transition metal oxides and produces hydroxyl radicals from hydrogen peroxide. These highly reactive hydroxyl radicals are responsible for degrading the organic pollutants through oxidation. The size [7,8], shape [9], and phase [10], of transition metal oxide particles can influence the characteristics and application performance of the particles. Liang et al.[11] have found that the pH during the iron oxide catalyst preparation influenced the morphology and the resulting photo-Fenton activity. In this study the Co_3O_4 nanoparticles prepared at different pH values were employed as catalysts to degrade methylene blue by the Fenton reaction.

2. Experimental

2.1. Materials

Methanol (CH_3OH, 99.8%) and cobalt acetate ($Co(CH_3COO)_2.4H_2O$, 99.99%) were purchased from Sigma-Aldrich[TM]. Sodium hydroxide (NaOH, 99%) and ethanol (CH_3CH_2OH, 99 %) was obtained from Glass World[TM] and hydrochloric acid (HCl, 32%) from Laboratory Consumables & Chemicals[TM]. Distilled water was used to prepare the solutions and all chemicals were used as received without further purification.

2.2. Preparation of cobalt oxide nanoparticles

In this study cobalt acetate has been chosen as a cobalt precursor since it has been shown that carboxylate ions favour the formation of cubic shaped nanoparticles[6] [12]. Cobalt (II) acetate tetrahydrate (4.99 g) were dissolved in 10 ml of distilled water. The cobalt acetate solution was added drop wise to a NaOH solution (100 ml of 0.2 M) in a three necked flask while stirring with a magnetic stirrer at room temperature. A blue precipitate formed, and the pH of the mixture was 8.5. The mixture was heated to 80-85 °C and was kept at this temperature for 72 hours under reflux. Air was bubbled at 193 ml/min through a 10-20 µm gas dispersion tube through the mixture to oxidise the cobalt hydroxide to cobalt oxide. The colour of the precipitate changed from blue to black. The mixture was cooled, and the particles were flocculated using 50 ml of ethanol. The solid particles were separated by centrifugation for 5 minutes at 5000 rpm. The particles were washed three times with 2 M hydrochloric acid to dissolve the unreacted cobalt hydroxide. Thereafter, the particles were washed twice with distilled water and once with methanol to aid with air drying of the particles. Different concentrations of NaOH [0.3 M (measured pH 8.4), 0.4 M (measured pH 10.2) and 0.7 M (measured pH 12.3)] were used for the preparation of other batches of particles.

2.3. Characterization

The XRD patterns were obtained with a Bruker D2 (D2-205530) diffractometer using secondary graphite monochromated CuKα radiation with a voltage setting of 30 kV and a current setting of 30 mA. The size and shape of the nanoparticles were determined using a LEO TEM 912 with an acceleration voltage of 120 kV and a tungsten wire filament. UV-Vis spectroscopic analyses were performed with a double beam spectrometer-Perkin Elmer Lambda 25 UV/Vis.

2.4. Fenton catalytic decolourisation testing

Reactions were carried out in a 250 ml beaker covered with foil to prevent photocatalysis. A mass of 0.01 g of cobalt oxide nanoparticles was dispersed in 50 ml of distilled water and sonicated for 30 minutes using an ultrasonic bath and thereafter 10 mL of methylene blue stock solution (1000 ppm) and 20 mL of distilled water were added and stirred with a magnetic stirrer at 500 rpm until a temperature of 38 °C was reached. The mixture was stirred continuously for 1 hour for adsorption equilibrium to be reached. The reaction was started with the addition of 20 ml of H_2O_2 (30%). Samples (1 mL) were taken at different times. Isopropanol (1 mL) were added to the sample and diluted with cold water to 100 mL in a volumetric flask. The isopropanol was added to quench the reaction. The diluted sample solution was centrifuged to remove the cobalt oxide particles. The diluted sample was analysed by UV-Vis spectroscopy.

3. Results and discussion

The optical properties of the nanoparticles were characterised using UV-Vis spectroscopy (Figure 1). The peak around 450 nm and 725 nm can be ascribed to the ligand to metal charge transfer of $Co^{3+}\leftarrow O^{2-}$ and $Co^{2+}\leftarrow O^{2-}$ respectively [6]. The particles prepared using 0.2 M to 0.4 M of NaOH had both ligand to metal charge transfer peaks. In contrast, at a NaOH concentration of 0.7 M, only one ligand to metal charge transfer peak was observed which may indicate that only one cobalt oxidation state, cobalt (III), was present and thus a different phase had formed at a high NaOH concentration. The peak below 300 nm may be due to π bonding–π anti-bonding electronic transition between the cobalt and oxygen (Co=O)[13].
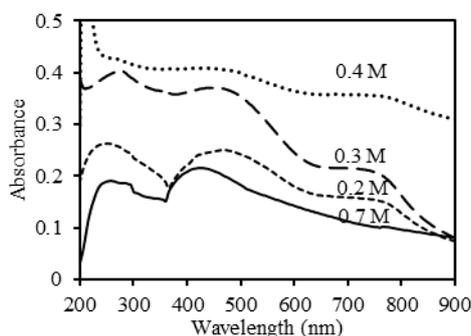
Fig. 1. UV-Vis spectra of Co₃O₄ nanoparticles synthesized from (a) 0.2 M, (b) 0.3 M, (c) 0.4 M and (d) CoOOH synthesized from 0.7 M of NaOH.

The diffraction patterns (Fig. 2a) for the nanoparticles that had been prepared using 0.2, 0.3, and 0.4 M of NaOH, were indexed to the face-centered cubic (fcc) phase of Co_3O_4 (PDF card number 03-065-3103). The lower concentrations of NaOH (0.2 M and 0.3 M) yielded two sets of diffractions peaks for the same phase of Co_3O_4 (Fig. 1(a-b)). The two sets of diffraction peaks could not be explained by any other cobalt oxide phase. The ratio of the first to second set of diffraction peaks decreased with an increase in the NaOH concentration (Figure 2b). Only one set of diffraction peaks for Co_3O_4 remained when sufficient NaOH was used to form $Co(OH)_2$ (Fig. 2). Previous research results showed that cobalt hydroxyl nitrate $(Co^{II}(OH)_{2-x}(NO_3)_x\bullet H_2O)$ or hydrotalcite $(Co^{II}_{1-x}Co^{III}_x(OH)_2(NO_3)_x\bullet nH_2O)$ intermediates formed when lower that the stoichiometric amount of hydroxide is used to form $Co(OH)_2$ (Equation 1) [14-16]. In this case nitrate ions are not present, but acetate ions are, since cobalt acetate was used as cobalt precursor and intermediates like $Co^{II}(OH)_{2-x}(O_2C_2H_3)_x\bullet H_2O$, or $(Co^{II}_{1-x}Co^{III}_x(OH)_2(O_2C_2H_3)_x\bullet nH_2O$ may have formed. The amount of the cobalt hydroxyl acetate/ hydrotalcite phases may be expected to decrease with an increase in the hydroxide concentration. The difference in intermediates may have resulted in the formation of Co_3O_4 with slightly different d-spacing and the first set of the double peaks may be due to Co_3O_4 formation from the cobalt hydroxyl acetate/ hydrotalcite phases since this set of peaks disappears with an increase in the NaOH concentration. The double peaks observed in the XRD diffraction pattern may be ascribed to uniform distortion or due to inherent strain of the lattice.

The particles prepared using the highest sodium hydroxide concentration (0.7 M) showed a different diffraction pattern with peaks corresponding to cobalt oxide hydroxide (heterogenite) phase, CoO(OH) (PDF card number 01-072-2280) (see Figure 2a). The phase identification of XRD is supported by the UV-Vis spectroscopy where only the peak for the ligand to metal charge transfer of $Co^{3+}\leftarrow O^{2-}$ was observed and ligand to metal charge transfer of $Co^{2+}\leftarrow O^{2-}$ was absent. The formation of CoO(OH) is in agreement with the previous research findings which reported its formation was favoured at high pH [14] [15] [17].
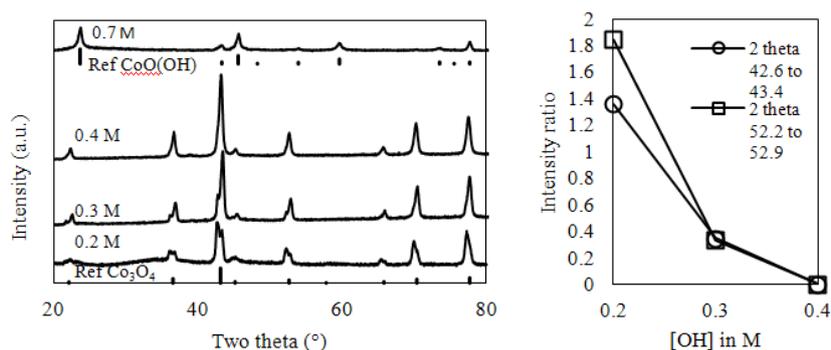
Fig. 2. (a) XRD pattern of nanoparticles prepared using different concentrations of NaOH. (b) The ratio of the first to second diffraction peaks indexed with (311) and (400) at 2θ values of ~42° and ~52° respectively.

The Co_3O_4 nanoparticles prepared with 0.2 M NaOH showed larger cubic nanoparticles (average size of 68.6 nm, standard deviation (σ) of 21.3 nm) as well as smaller undefined shapes (average of 45.7 nm, σ of 35.5 nm) (Fig. 3). Increasing the NaOH concentration to 0.3 M favoured the formation of well-defined cubic shaped nanoparticles, which showed a bi-modal distribution with an average of 51.9 nm and a standard deviation of 21.8 nm (Figure 3). A small number of spherical particles with an average diameter of 21.9 nm and a standard deviation of 10.8 nm was also found to be present (Figure 3). The formation of different shapes and sizes of nanoparticles may arise from the different rates of oxidation of different cobalt precipitates i.e. $Co^{II}(OH)_{2-x}(O_2C_2H_3)_x \cdot H_2O$, $(Co^{II}_{1-x}Co^{III}_x(OH)_2(O_2C_2H_3)_x \cdot nH_2O$ and β-$Co(OH)_2$ due to the use lower amounts of hydroxyl ions required to form $Co(OH)_2$.

At a NaOH concentration of 0.4 M, which provided the stoichiometric amount of hydroxyl ions to form $Co(OH)_2$ (see Equation 1), well defined cubic shaped nanoparticles with a narrower mono-modal size distribution were formed (as seen in Figure 3). The average size was 32.4 nm with a standard deviation of 4.3 nm. The nanoparticles prepared using 0.4 M NaOH were more agglomerated and smaller than the nanoparticles prepared with 0.3 M NaOH. An increase in agglomeration with an increase in pH was also previously observed and it was explained by an increase in the rate of the condensation reaction of $Co(OH)_2$ (see Equation 2). This possibly caused the nanoparticles to be linked together resulting in agglomeration [12].

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \qquad (1)$$

$$\text{-Co-OH} + \text{H-O-Co} \rightarrow \text{-Co-O-Co-} + H_2O \qquad (2)$$
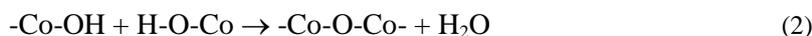
The sizes calculated from the XRD diffraction patterns using the Scherrer equation yielded significantly smaller sizes than those measured from the TEM micrographs (Table 1). This discrepancy may be explained by cracks observed in the particles as shown in the zoomed-in section of the nanoparticles prepared using 0.3 M NaOH (Figure 3). This supports the explanation offered earlier, that the condensation reaction of $Co(OH)_2$ (see Equation 2) may be linking particles together.

The particles prepared from 0.7 M of NaOH showed a mixture of rods, sphere-like, cube-like and rectangular shapes (Fig. 4).

Table 1. Nanoparticle size comparison between XRD and TEM.

NaOH concentration/ M	Co$_3$O$_4$ XRD size using (311) peaks/nm	CoOOH XRD size using (110) peak/nm	TEM size/nm
0.2	15.5 ;16.9		68.6 (cubic); 45.7(others)
0.3	14.9; 17.2		51.9 (cubic); 21.9 (others)
0.4	11.8		32.4 (cubic)
0.7		9.9	
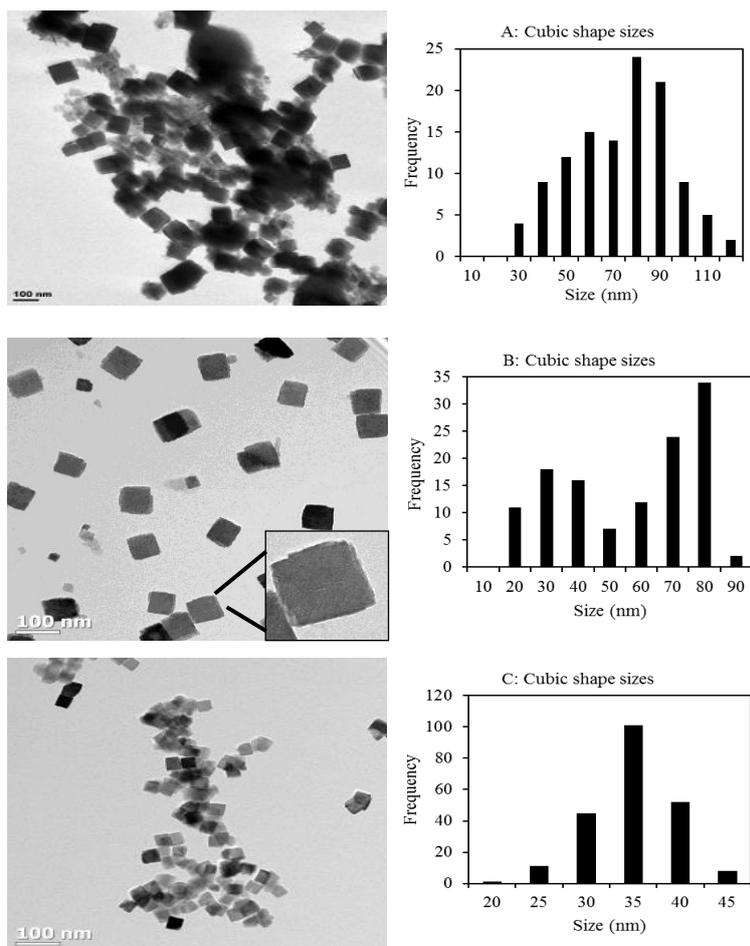
Fig. 3. TEM images and size distribution of Co$_3$O$_4$ nanocubes prepared from (a) 0.2 M, (b) from 0.3 M (c) 0.4 M of NaOH
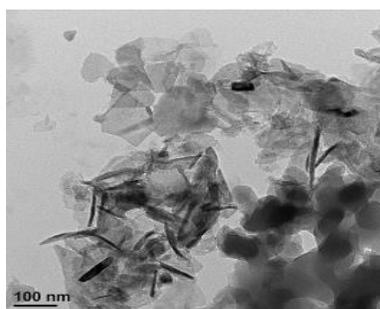
Fig. 4. TEM images of CoOOH particles of different morphologies prepared from 0.7 M of NaOH.

The Fenton catalytic degradation was subsequently studied by using the cubic shaped Co_3O_4 nanoparticles as catalysts as shown in Figure 5. The highest decolourisation percentages were obtained with cobalt oxide particles prepared from 0.3 M of NaOH whereas relatively low efficiencies in degradation were found in particles prepared from 0.2 M and 0.4 M NaOH. The measurement for 0.3M NaOH was repeated in order to ascertain the procedure and confirm the findings. The higher activity of the Co_3O_4 nanoparticles prepared using 0.3 M NaOH may be explained by the lower amount of agglomeration found in this sample. The expectation was that the smallest nanoparticles would result in the highest activity due to a higher metal oxide surface area [8], however, the surface area is not only governed by size, but also by the dispersion of nanoparticles in the reaction solution. Pseudo first order rate constants of 0.06 min^{-1} was obtained for the nanoparticles prepared using 0.3 M of NaOH (Fig. 5).
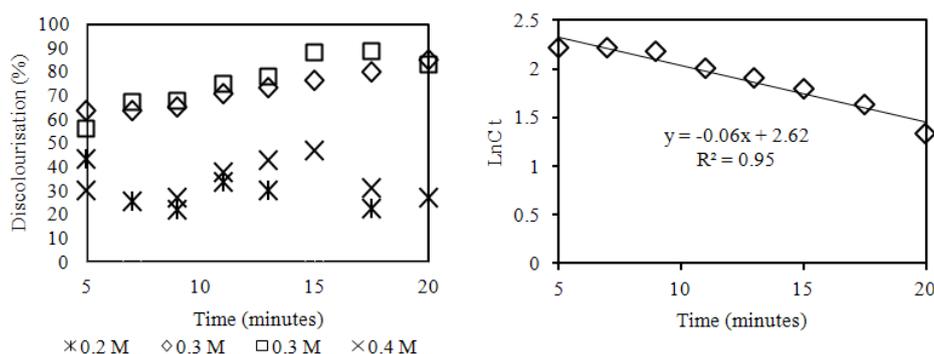
Fig. 5. Fenton decolourisation of methylene blue by Co_3O_4 and CoOOH nanoparticles: (a) % decolourisation (b) Pseudo first order reaction kinetics.

4. Conclusions

The concentration of sodium hydroxide used during the experimental preparation of the cobalt oxide nanoparticles influenced the size, shape, agglomeration and phase of the cobalt oxide nanoparticles. A mixture of cubic shaped and undefined Co_3O_4 nanoparticles formed at the lowest NaOH concentration. The number well-defined cubic shaped Co_3O_4 nanoparticles increased when higher NaOH concentrations were used. Various crystal shapes formed at the highest NaOH concentration. Using less than the required stoichiometric amounts of NaOH lead to the formation of a mixture of Co_3O_4 with two slightly different diffraction angles.

The nanoparticles that formed when a stoichiometric amount of NaOH was used, had one set of lattice spacings that corresponded to the reference XRD spectrum of Co_3O_4. CoO(OH) formed when a high concentration of 0.7 M of NaOH was used. The Co_3O_4 nanoparticles that had been prepared using 0.3 M NaOH were more catalytically active than the Co_3O_4 nanoparticles prepared at 0.2 M and 0.4 M. The Co_3O_4 nanoparticles that were prepared using 0.3 M NaOH were the least agglomerated in comparison to the other nanoparticles, which may explain their higher observed Fenton catalytic activity.

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