Chapter IV

Results
INTRODUCTION:

This section includes the characterization of Co$_3$O$_4$, CuO and Co$_3$O$_4$/CuO nanostructures synthesized via different methods.

4.1 Chemical combustion synthesis and characterization of Co$_3$O$_4$, CuO and Co$_3$O$_4$/CuO nanostructure:

Chemical combustion synthesis is an effective method for the synthesis of nanoscale materials and has been used in the production of various powders for a variety of advanced applications. Oxide powders at the nanoscale using Chemical combustion synthesis can be prepared by the combination of metal nitrates in an aqueous solution with a fuel. The properties of the resulting powders (crystalline structure, amorphous structure, crystallite size, purity, specific surface area and particle agglomeration) depend heavily on the adopted processing parameters.

The experimental methodology has been explained in detail in Chapter III. Following is the detail of the characterized samples of Co$_3$O$_4$, CuO and Co$_3$O$_4$/CuO synthesized via chemical combustion method and annealed at 400°, 500° and 600°C.

4.1.1 Co$_3$O$_4$:

4.1.1.1 XRD of Co$_3$O$_4$:

Figure 4.1.1.1(a) shows the XRD pattern of Co$_3$O$_4$ samples taken after annealing at 400°, 500° and 600°C. XRD graphs indicate the formation of polycrystalline spinel phase. All diffraction peaks in this pattern could be indexed to a cubic spinel Co$_3$O$_4$ with lattice parameter a = 8.083 Å (JCPDS No. 42-1467).
The peaks at 2θ = 19.01°, 31.37°, 36.88°, 38.56°, 44.84°, 55.67°, 59.39°, and 65.25° corresponding to (111), (220), (311), (222), (400), (422), (511), and (440) reflections of cubic spinel Co₃O₄ with Fd3m [227] space group. No obvious peaks of impurities due to CoO, CoO₂ and Co were seen in the pattern of the sample annealed at 600°C. Results indicated increase in crystallite size with the increase in annealing temperature as shown in figure 4.1.1.1(b).
The average crystallite sizes for the most intense peak [(311) plane] calculated from the XRD data using Debye-Scherer formula were 14, 17 and 21nm for Co$_3$O$_4$ nanostructures at 400°, 500° and 600°C respectively.

4.1.1.2 FTIR of Co$_3$O$_4$:

The FTIR spectrum of the Co$_3$O$_4$ nanostructures synthesized via chemical combustion method and annealed at 400°, 500° and 600°C are shown in Figure 4.1.1.2.

![FTIR spectra of Co$_3$O$_4$ nanostructures at 400°, 500° and 600°C](image)

**FIGURE 4.1.1.2: FTIR spectra of Co$_3$O$_4$ nanostructures at 400°, 500° and 600°C**

The figure clearly represents the metal-oxygen absorption band, characteristic of cubic spinel structure of Co$_3$O$_4$. The broad absorption bands at about 3419.60 cm$^{-1}$, 3446.48 cm$^{-1}$ and 3430.28 cm$^{-1}$ represents the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.

4.1.1.3 TEM of Co$_3$O$_4$:

The TEM images for the Co$_3$O$_4$ nanostructures synthesized via chemical combustion method are shown in Figure 4.1.1.3 (a) 400°C, (b) 500°C and (c) 600°C. The micrographs show uniformity in shape and size. The particle sizes were found to be
14, 17 and 21 nm for the annealed samples at 400°, 500° and 600°C respectively. There is good consistency between the values observed by TEM and XRD.

**FIGURE 4.1.1.3:** TEM images of Co₃O₄ nanostructures at (a) 400°C, (b) 500°C and (c) 600°C

### 4.1.2 CuO:

#### 4.1.2.1 XRD of CuO:

Figure 4.1.2.1(a) shows the XRD pattern of CuO samples taken after annealing at 400°, 500° and 600°C. All diffraction peaks in this pattern could be indexed to a pure monoclinic (Tenorite) crystalline CuO with lattice parameters \( a = 4.68370 \text{ Å} \), \( b = 3.42260 \text{ Å} \), \( c = 5.12880 \text{ Å} \) and \( \beta = 99.540 \) (JCPDS No. 72-0629). No obvious peaks
of impurities were seen in this pattern such as Cu$_2$O, Cu, Cu(NO$_3$)$_2$, etc. in the sample annealed at 600°C

![XRD pattern of Co$_3$O$_4$ nanostructures at 400°C, 500°C and 600°C](image)

**FIGURE 4.1.2.1(a):** XRD pattern of Co$_3$O$_4$ nanostructures at 400°C, 500°C and 600°C

The peaks at $2\theta = 32.55^\circ$, $35.57^\circ$, $38.73^\circ$, $47.49^\circ$, $48.80^\circ$, $51.48^\circ$, $53.51^\circ$, $58.22^\circ$, $61.56^\circ$, $65.85^\circ$, $66.29^\circ$ and $68.09^\circ$ correspond to (110), (̅111), (111), (̅112), (̅202), (112), (020), (202), (̅113), (022), (̅311) and (220) reflections of the monoclinic crystalline CuO with space group C2/c [15]. Results indicated increase in crystallite size with the increase in annealing temperature.

![Graph between crystallite size and temperature](image)

**FIGURE 4.1.2.1(b):** Graph between crystallite size and temperature
The average crystallite sizes for the most intense peak calculated from the XRD data using Debye-Scherer formula were 24, 27 and 29 nm for CuO nanostructures at 400°, 500° and 600°C respectively.

4.1.2.2 FTIR of CuO:

The FTIR spectrum of the CuO nanostructures synthesized via chemical combustion method and annealed at 400°, 500° and 600°C is shown in Figure 4.1.2.2.

FIGURE 4.1.2.2: FTIR spectra of CuO nanostructures at 400°, 500° and 600°C

The figure clearly represents the metal-oxygen absorption band, characteristic of monoclinic CuO. The broad absorption bands near 3420.31 cm\(^{-1}\) represent the stretching mode of H\(_2\)O molecule and OH groups with other minor absorption bands.

4.1.2.3: TEM of CuO:

The TEM images for the CuO nanostructures synthesized via chemical combustion method are shown in Figure 4.1.2.3 (a) 400°C, (b) 500°C and (c) 600°C. The micrograph shows uniformity in shape and size. The particle sizes were found to
be 24, 27 and 29 nm for the annealed samples at 400°, 500° and 600°C respectively. There is good consistency between the values observed by TEM and XRD.

![TEM images of CuO nanostructures at (a) 400°C, (b) 500°C and (c) 600°C](image)

**FIGURE 4.1.2.3: TEM images of CuO nanostructures at (a) 400°C, (b) 500°C and (c) 600°C**

4.1.3 Co$_3$O$_4$/CuO:

4.1.3.1 XRD of Co$_3$O$_4$/CuO:

Figure 4.1.3.1 shows the XRD pattern of Co$_3$O$_4$/CuO samples taken after annealing at 400°, 500° and 600°C. XRD pattern of the nanostructures revealed the presence of both a cubic spinel Co$_3$O$_4$ with lattice parameter $a = 8.083$ Å (JCPDS No. 42-1467) and a pure monoclinic crystalline CuO with lattice parameters $a = 4.68370$ Å, $b = 3.42260$ Å, $c = 5.12880$ Å and $\beta = 99.540$ (JCPDS No. 72-0629).
No obvious peaks of impurities such as CuO, Cu₂O, CoO, CoO₂, Cu, Co, Cu, Cu(NO₃)₂, etc. were observed seen in the pattern annealed at 600°C.

FIGURE 4.1.3.1: XRD pattern of Co₃O₄/CuO nanostructures at 400°, 500° and 600°C

The peaks at 2θ = 19.17°, 31.46°, 37.02°, 44.90°, 55.80°, 59.54° and 65.39° correspond to (111), (220), (311), (400), (422), (511), and (440) reflections of the cubic spinel Co₃O₄ with Fd3m space group and the peaks at 2θ = 32.73°, 35.78°, 38.94°, 47.76°, 48.87°, 53.80°, 58.44°, 61.73°, 65.59°, 66.31° and 68.42° corresponds to (110), (111), (111), (112), (202), (202), (113), (022), (311) and (220) reflections of the monoclinic crystalline CuO with space group C2/c [15]. Results indicated increase in crystallite size with the increase in annealing temperature.

The average crystallite sizes for the most intense peak calculated from the XRD data using Debye-Scherer formula were 455 nm, 47 nm and 36 nm for Co₃O₄ nanostructures at 400°, 500° and 600°C respectively.

4.1.3.2 FTIR of Co₃O₄/CuO:

The FTIR spectrum of the Co₃O₄/CuO nanostructures synthesized via chemical combustion method and annealed at 400°, 500° and 600°C is shown in Figure 4.1.3.2. The figure clearly represents the Metal-oxygen absorption bands, characteristic of cubic spinel structure of Co₃O₄ and monoclinic CuO. The broad
absorption bands near 3400 cm\(^{-1}\) represent the stretching mode of H\(_2\)O molecule and OH groups with other minor absorption bands.

**FIGURE 4.13.2:** FTIR spectrum of Co\(_3\)O\(_4\)/CuO nanostructures at 400\(^\circ\)C, 500\(^\circ\)C and 600\(^\circ\)C

### 4.1.3.3 TEM of Co\(_3\)O\(_4\)/CuO:

The TEM images for the CuO nanostructures synthesized via chemical combustion method are shown in Figure 4.1.2.3 (a) 400\(^\circ\)C, (b) 500\(^\circ\)C and (c) 600\(^\circ\)C.
FIGURE 4.1.3.3: TEM images of Co$_3$O$_4$/CuO nanostructures at (a) 400°C, (b) 500°C and (c) 600°C

The micrograph shows uniformity in shape and size. The Figures represent rod like structures with diameter ~ 31 nm and length 455 nm at 400°C whereas almost cubic particles are observed at 500°C and 600°C with average diameter 47 ± 1 nm and 36 ± 1 nm respectively. There is a good consistency between the values observed by TEM and XRD.

4.2 Sol-gel auto combustion synthesis and characterization of Co$_3$O$_4$, CuO and Co$_3$O$_4$/CuO nanostructure:

The experimental methodology has been explained in detail in chapter 3. Following is the detail of the characterized samples of Co$_3$O$_4$, CuO and Co$_3$O$_4$/CuO synthesized via sol-gel auto combustion synthesis and annealed at 450°C.
4.2.1 Co$_3$O$_4$:

4.2.1.1 XRD of Co$_3$O$_4$:

Figure 4.2.1.1 shows the XRD pattern of Co$_3$O$_4$ samples taken after annealing at 450°C. XRD graph indicates the formation of polycrystalline spinel phase. All diffraction peaks in this pattern could be indexed to a cubic spinel Co$_3$O$_4$ with lattice parameter $a = 8.083$ Å (JCPDS No. 42-1467).

![XRD pattern](image)

**FIGURE 4.2.1.1: XRD pattern of Co$_3$O$_4$ nanostructure at 450°C**

In Figure 4.2.1.1, peaks at $2\theta = 19.08^\circ$, $31.34^\circ$, $36.91^\circ$, $38.61^\circ$, $44.92^\circ$, $55.73^\circ$, $59.42^\circ$ and $65.30^\circ$ are attributed to (111), (220), (311), (222), (400), (422), (511) and (440) reflections of the cubic structure of the spinel with Fd3m space group. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 39 nm.

4.2.1.2 FTIR of Co$_3$O$_4$:

The FTIR spectrum of the Co$_3$O$_4$ nanostructure synthesized via sol-gel autocombustion method and annealed at 450°C is shown in Figure 4.2.1.2.
FIGURE 4.2.1.2: FTIR spectrum of Co$_3$O$_4$ nanostructure at 450°C

The figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co$_3$O$_4$. The broad absorption bands near 3397.18 cm$^{-1}$ represents the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.

4.2.1.3 TEM of Co$_3$O$_4$:

The TEM image for the Co$_3$O$_4$ nanostructure synthesized via sol-gel auto-combustion method and annealed at 450°C is shown in Figure 4.2.1.3. The micrograph shows agglomeration of particles. The particle sizes were found to be 39 ± 2 nm for the annealed sample. There is a good consistency between the values observed by TEM and XRD.
4.2.2 CuO:

4.2.2.1 XRD of CuO:

Figure 4.2.2.1 shows the XRD pattern of CuO sample synthesized via sol-gel auto-combustion method annealed at 450°C. All diffraction peaks in this pattern could be indexed to a pure monoclinic (Tenorite) crystalline CuO with lattice parameters $a = 4.68370 \, \text{Å}$, $b = 3.42260 \, \text{Å}$, $c = 5.12880 \, \text{Å}$ and $\beta = 99.540$ (ICDD card No. 72-0629). No obvious peaks of impurities were seen in this pattern such as Cu$_2$O, Cu, Cu(NO$_3$)$_2$, etc.
The peaks at $2\theta = 32.56^\circ, 35.61^\circ, 38.77^\circ, 47.54^\circ, 48.88^\circ, 51.35^\circ, 53.54^\circ, 58.35^\circ, 61.62^\circ, 65.92^\circ, 66.34^\circ$ and $68.14^\circ$ correspond to (110), ($\bar{1}11$), (111), ($\bar{1}12$), (020), (202), ($\bar{1}13$), (022), ($\bar{3}11$) and (220) reflections of the monoclinic crystalline CuO with space group C2/c[15]. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 32 nm.

4.2.2.2 FTIR of CuO:

The FTIR spectrum of the CuO nanostructure synthesized via sol-gel autocombustion method and annealed at 450°C is shown in Figure 4.2.2.2.

FIGURE 4.2.2.2: FTIR spectrum of CuO nanostructure at 450°C

The figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co$_3$O$_4$. The broad absorption bands near 3400 cm$^{-1}$ represent the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.
4.2.2.3 TEM of CuO:

The TEM image for the CuO nanostructure synthesized via sol-gel autocombustion method and annealed at 450°C is shown in Figure 4.2.2.3. The micrograph shows agglomeration of the particles. The particle sizes were found to be 32 ±1 nm for the annealed sample. There is good consistency between the values observed by TEM and XRD.

![TEM image of CuO nanostructure at 450°C](image)

**FIGURE 4.2.2.3: TEM image of CuO nanostructure at 450°C**

4.2.3 Co$_3$O$_4$/CuO:

4.2.3.1 XRD of Co$_3$O$_4$/CuO:

Figure 4.2.3.1 shows the XRD pattern of Co$_3$O$_4$/CuO sample synthesized via sol-gel autocombustion method annealed at 450°C. XRD pattern of the nanostructures revealed the presence of both a cubic spinel Co$_3$O$_4$ with lattice parameter $a = 8.083$ Å (JCPDS No. 42-1467) and a pure monoclinic crystalline CuO with lattice parameters $a = 4.68370$ Å, $b = 3.42260$ Å, $c = 5.12880$ Å and $β = 99.540$ (JCPDS No. 72-0629). No obvious peaks of impurities were seen in this pattern such as CuO, Cu$_2$O, CoO, CoO$_2$, Cu, Co, Cu, Cu(NO$_3$)$_2$, etc. in the sample annealed at 450°C.
FIGURE 4.2.3.1: XRD pattern of Co$_3$O$_4$/CuO nanostructure at 450°C

The peaks at 2θ = 19.10°, 31.39°, 36.95°, 44.85°, 55.78°, 59.47° and 65.32° correspond to (111), (220), (311), (400), (422), (511), and (440) reflections of the cubic spinel Co$_3$O$_4$ with Fd3m space group and the peaks at 2θ =32.63°, 35.66°, 38.82°, 47.10°, 48.88°, 50.36°, 53.66°, 58.52°, 61.62°, 65.87°, 66.29° and 68.40° correspond to (110), (111), (112), (202), (112), (020), (202), (113), (022), (311) and (220) reflections of the monoclinic crystalline CuO with space group C2/c [15]. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 71 nm.

4.2.3.2 FTIR of Co$_3$O$_4$/CuO:

The FTIR spectrum of the Co$_3$O$_4$/CuO nanostructures synthesized via sol-gel auto-combustion method and annealed at 450°C is shown in Figure 4.2.3.2.
FIGURE 4.2.3.2: FTIR spectrum of Co$_3$O$_4$/CuO nanostructure at 450°C

The figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co$_3$O$_4$ and monoclinic CuO. The broad absorption bands near 3400 cm$^{-1}$ represent the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.

4.2.3.3 TEM of Co$_3$O$_4$/CuO:

The TEM image for the Co$_3$O$_4$/CuO nanostructure synthesized via sol-gel autocombustion method and annealed at 450°C is shown in Figure 4.2.3.3. The micrograph shows uniformity in shape and size. The particle sizes were found to be 73 ±2 nm for the annealed sample. There is a good consistency between the values observed by TEM and XRD.
4.3 Hydrothermal synthesis and characterization of Co$_3$O$_4$ nanostructures:

The experimental methodology has been explained in detail in Chapter III. Following is the detail of the characterized samples of Co$_3$O$_4$ synthesized via hydrothermal synthesis.

4.3.1 Co$_3$O$_4$ (Ethanol:Water):

4.3.1.1 XRD of Co$_3$O$_4$ (Ethanol:Water):

Figure 4.3.1.1 shows the XRD pattern of Co$_3$O$_4$ samples synthesized via hydrothermal method using water:ethanol mixture as solvent. XRD graph indicate the formation of polycrystalline spinel phase. The diffraction peaks in this pattern could be indexed to a cubic spinel Co$_3$O$_4$ with lattice parameter $a = 8.083$ Å (JCPDS No. 42-1467).
In Figure 4.3.1.1, peaks at $2\theta = 19.15^\circ$, $31.47^\circ$, $37.00^\circ$, $38.78^\circ$, $44.94^\circ$, $55.89^\circ$, $59.54^\circ$ and $65.47^\circ$ are attributed to (111), (220), (311), (222), (400), (422), (511) and (440) reflections of the cubic structure of the spinel with Fd3m space group. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 28 nm.

4.3.1.2 FTIR of $\text{Co}_3\text{O}_4$ (Ethanol:Water):

The FTIR spectrum of the $\text{Co}_3\text{O}_4$ nanostructure synthesized via hydrothermal method using ethanol:water mixture as solvent is shown in Figure 4.3.1.2.
FIGURE 4.3.1.2: FTIR spectrum of Co$_3$O$_4$ (Ethanol:Water) nanostructure

The figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co$_3$O$_4$. The broad absorption bands near 3400 cm$^{-1}$ represents the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.

4.3.1.3 TEM of Co$_3$O$_4$ (Ethanol:Water):

The TEM image for the Co$_3$O$_4$ nanostructure synthesized via hydrothermal method using ethanol:water mixture as solvent is shown in Figure 4.3.1.3. The micrograph shows uniformity in shape and size. The particle sizes were found to be 28 ±2 nm for the annealed sample. There is good consistency between the values observed by TEM and XRD.
4.3.2 Co$_3$O$_4$ (Water):

4.3.2.1 XRD of Co$_3$O$_4$ (Water):

Figure 4.3.2.1 shows the XRD pattern of Co$_3$O$_4$ samples synthesized via hydrothermal method using water as solvent. XRD graph indicate the formation of polycrystalline spinel phase. The diffraction peaks in this pattern could be indexed to a cubic spinel Co$_3$O$_4$ with lattice parameter a = 8.083 Å (JCPDS No. 42-1467).

FIGURE 4.3.2.1: XRD pattern of Co$_3$O$_4$ (water) nanostructure
In Figure 4.3.2.1, peaks at $2\theta = 19.50^\circ, 31.83^\circ, 37.34^\circ, 38.99^\circ, 45.34^\circ, 56.04^\circ, 59.73^\circ$ and $65.64^\circ$ are attributed to (111), (220), (311), (222), (400), (422), (511) and (440) reflections of the cubic structure of the spinel with Fd3m space group. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 21 nm.

4.3.2.2 FTIR of Co$_3$O$_4$ (water):

The FTIR spectrum of the Co$_3$O$_4$ nanostructure synthesized via hydrothermal method using water as solvent is shown in Figure 4.3.2.2.

![FTIR spectrum of Co$_3$O$_4$ (Water) nanostructure](image)

**FIGURE 4.3.2.2: FTIR spectrum of Co$_3$O$_4$ (Water) nanostructure**

The figure clearly represents the metal-oxygen absorption bands, characteristic of cubic spinel structure of Co$_3$O$_4$. The broad absorption bands near 3400 cm$^{-1}$ represents the stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.
4.3.2.3 TEM of Co$_3$O$_4$ (water):

The TEM image for the Co$_3$O$_4$ nanostructure synthesized via hydrothermal method using water as solvent is shown in Figure 4.3.2.3. The micrograph shows uniformity in shape and size. The particle sizes were found to be 21 ±1nm for the annealed sample. There is good consistency between the values observed by TEM and XRD.

![TEM Image of Co$_3$O$_4$ (Water) nanostructure](image)

**FIGURE 4.3.2.3: TEM image of Co$_3$O$_4$ (Water) nanostructure**

4.4 Thermal decomposition synthesis and characterization of Co$_3$O$_4$

nanostructure:

The experimental methodology has been explained in detail in chapter 3. Following is the detail of the characterized samples of Co$_3$O$_4$ synthesized via thermal decomposition method.

4.4.1 Co$_3$O$_4$

4.4.1.1 XRD of Co$_3$O$_4$:

Figure 4.4.1.1 shows the XRD pattern of Co$_3$O$_4$ take after the thermal decomposition of cobalt hydroxy carbonates. From the XRD pattern, it was observed that a polycrystalline phase was formed. All diffraction peaks in this pattern could be indexed to a cubic spinel Co$_3$O$_4$ with lattice parameter $a = 8.083$ Å (JCPDS No. 42-1467).
FIGURE 4.4.1.1: XRD pattern of Co$_3$O$_4$ nanostructure

In Figure 4.4.1.1, peaks at 2θ = 19.07°, 31.37°, 36.93°, 38.66°, 44.86°, 55.77°, 59.47° and 65.32° are attributed to (111), (220), (311), (222), (400), (422), (511) and (440) reflections of the cubic structure of the spinel with Fd3m space group. The lattice parameter was calculated, i.e, $a$(Å) $\sim$ 8.066. The average crystalline size was calculated from the XRD data using Debye-Scherer formula and was found to be 16 ± 1 nm.

4.4.1.2 FTIR of Co$_3$O$_4$:

The FTIR spectrum of the Co$_3$O$_4$ is shown in Figure 4.4.1.2. Spectrum clearly shows the metal-oxygen absorption band, characteristic of cubic spinel structure.
FIGURE 4.4.1.2: FTIR spectrum of Co$_3$O$_4$ nanostructure

A broad absorption band at about 3433.09 cm$^{-1}$ represents stretching mode of H$_2$O molecule and OH groups with other minor absorption bands.

4.4.1.3 TEM of Co$_3$O$_4$:

Figure 4.4.1.3 represents the surface morphology in terms of micrograph (TEM image) for Co$_3$O$_4$ sample. The micrograph shows uniformity in shape and size. The particle size was found to be 16 ± 1 nm. There is good consistency between the values observed by TEM and XRD.
4.5 Catalytic oxidation observations:

4.5.1 Oxidation of formaldehyde:

Figure 4.5.1 represents the oxidation of 1% HCHO using the synthesized nanocatalysts at 20º, 30º and 40ºC where Co₃O₄-CC, CuO-CC, Co₃O₄/CuO-CC, Co₃O₄-SGA, CuO-SGA, Co₃O₄/CuO-SGA, Co₃O₄-HT(W), Co₃O₄-HT(E) and Co₃O₄-TD represents Co₃O₄ synthesized by chemical combustion, CuO synthesized by chemical combustion, Co₃O₄/CuO synthesized by chemical combustion, Co₃O₄ synthesized by sol-gel autocombustion, CuO synthesized by sol-gel autocombustion, Co₃O₄/CuO synthesized by sol-gel autocombustion, Co₃O₄ (Water) synthesized by hydrothermal, Co₃O₄ (Ethanol) synthesized by hydrothermal and Co₃O₄ synthesized by thermal decomposition methods respectively.
FIGURE 4.5.1: Oxidation of formaldehyde by nanocatalysts at 20°, 30° and 40°C

The graph indicates the oxidative nature of nanocatalysts and also gives the information regarding comparative oxidation study of the respective nanocatalyst. The results for the titration were recorded and are shown in Table 4.5.1 below.

TABLE 4.5.1: Titration results for the oxidation of formaldehyde by nanocatalysts at 20°, 30° and 40°C

<table>
<thead>
<tr>
<th>S.No</th>
<th>Catalyst</th>
<th>20°C (in ml)</th>
<th>30°C (in ml)</th>
<th>40°C (in ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without catalyst</td>
<td>15</td>
<td>13</td>
<td>9.8</td>
</tr>
<tr>
<td>2</td>
<td>Co3O4 - TD</td>
<td>6.7</td>
<td>5.8</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>Co3O4 - CC</td>
<td>10.4</td>
<td>8.8</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>CuO - CC</td>
<td>9.8</td>
<td>8.6</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>Co3O4/CuO - CC</td>
<td>8.6</td>
<td>6.9</td>
<td>4.9</td>
</tr>
<tr>
<td>6</td>
<td>Co3O4 - SGA</td>
<td>7.3</td>
<td>6.6</td>
<td>5.4</td>
</tr>
<tr>
<td>7</td>
<td>CuO - SGA</td>
<td>8.7</td>
<td>7.0</td>
<td>5.0</td>
</tr>
<tr>
<td>8</td>
<td>Co3O4/CuO - SGA</td>
<td>8.8</td>
<td>7.3</td>
<td>5.1</td>
</tr>
<tr>
<td>9</td>
<td>Co3O4 – HT (W)</td>
<td>7.7</td>
<td>6.1</td>
<td>4.0</td>
</tr>
<tr>
<td>10</td>
<td>Co3O4 - HT (E)</td>
<td>8.2</td>
<td>7.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>
4.5.2 Oxidation of oxalic acid:

Figure 4.5.2 represents the oxidation of oxalic acid by Co$_3$O$_4$ nanocatalyst synthesized by thermal decomposition method. The lines in the figure represent the different sets of readings for the oxidation of oxalic acid by Co$_3$O$_4$ nanocatalyst at 25°, 35°, 45°, 55° and 65°C.

![Graph showing the oxidation of oxalic acid by Co$_3$O$_4$-TD at various temperatures.](image)

**FIGURE 4.5.2: Oxidation of oxalic acid by Co$_3$O$_4$-TD at 25°, 35°, 45°, 55° and 65°C**

The catalyst gives the best result at 65°C. The results for the oxidation of oxalic acid via titration were recorded and are shown in Table 4.5.2 below:

**Table 4.5.2 Titration results for the oxidation of oxalic acid by Co$_3$O$_4$ at 25°, 35°, 45°, 55° and 65°C**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>Reaction time (in minutes)</th>
<th>Result (in ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 25°C</td>
<td></td>
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At 35°C

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At 45°C

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At 55°C

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At 65°C

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<td>5</td>
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4.5.3 Oxidation of benzaldehyde:

Figure 4.5.3(a) represents the NMR graph for the selective oxidation of benzaldehyde to benzoic acid by Co$_3$O$_4$ nanocatalyst synthesized by thermal decomposition method.
FIGURE 4.5.3(b): NMR of benzoic acid
FIGURE 4.5.3(c): Position of \( H_a, H_b, H_c \) and \( H_d \) in benzoic acid

The data for the peaks of benzoic acid was calculated from the NMR spectra. The position of the hydrogens in benzoic acid is shown in Figure 4.5.3(b) where \( H_a, H_b, H_c \) and \( H_d \) are ortho, meta, para and carboxylic group protons.

\(^1\)HNMR (CDCl\(_3\)): \( \delta 7.45 - 7.48 \) (t, 2H, \( H_b \), \( J_o = 7.84 \) HZ)

\( \delta 7.58 - 7.63 \) (tt, 1H, \( H_c \), \( J_o = 7.4 \) and \( J_m = 1.12 \) Hz)

\( \delta 8.11 - 8.14 \) (dd, 2H, \( H_a \), \( J_o = 7.04 \) and \( J_m = 1.44 \) Hz)

\( \delta 12.17 \) (bs, 1H, \( H_d \))

The result for the NMR data of benzoic acid matches with the reported data in literature. Results regarding concentration, time and yield are shown in the Table 4.5.3 below:

**TABLE 4.5.3 Yield of benzoic acid obtained at different time periods**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Benzaldehyde</th>
<th>( \text{Co}_3\text{O}_4 ) nanocatalyst</th>
<th>Time</th>
<th>Benzoic acid(Yield)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2 ml</td>
<td>200mg</td>
<td>3hrs</td>
<td>35%</td>
</tr>
<tr>
<td>2</td>
<td>2 ml</td>
<td>200mg</td>
<td>4hrs</td>
<td>50%</td>
</tr>
<tr>
<td>3</td>
<td>2 ml</td>
<td>200 mg</td>
<td>6hrs</td>
<td>70%</td>
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