

## Controlled Method for Preparation and Characterization of Nanostructured Carbon Based Fe, Co -Containing Catalysts

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### Abstract

The iron, cobalt- carbon materials were synthesized as catalytic complex CTC and CTC modified chlorides of Fe (III), and Co (II) with controlled method. These catalytic complexes based on the reaction of aluminum and ethylene dichloride in liquid paraffin, and due to its composition and structure in comparison with the Friedel-Crafts catalysts, has a higher stable catalytic activity. The obtained xerogel (designated as CTC-110) was submitted to thermal treatment at 200, 400, 600, and 850 °C. and the resulting materials were characterized by means of different techniques, such as X-ray fluorescence microscopy (XRFM), thermal analyses (TG/DSC), X-ray diffractometer (XRD), and Dynamic light scattering analyses for particle size determination of the targeted samples. As a result, studies have shown that under given conditions the reaction of Al with dichloroethane leads to the improvement the carbon matrix, then after modifying this catalytic complex with different metal chloride (iron and cobalt) at different calcined temperatures leads also to modification in physical and chemical properties of the formed catalytic complexes and the different techniques which we used confirmed these results.

**Keywords:** Nanostructured materials, CTC, Fe/CTC, Co/CTC, XRFM.

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## 1. INTRODUCTION

Nanostructured materials exhibit different, often enhanced, magnetic, electronic, optical and reactive properties compared to corresponding bulk materials, making them desirable for applications including catalysis, adsorption, ferrofluids, electronic sensing, medical applications, and drug delivery [1-6]. For many applications, transition metals provide a distinct advantage over

precious metals because of their decreased costs. Interest in iron nanoparticles originates from iron's magnetic properties, its ready availability and low cost, and its high reactivity, particularly in reducing atmospheres [1, 7]. Specific applications for iron nanoparticles include Fischer–Tropsch catalysts, oxygen reduction catalysts in fuel cells, environmental adsorbents for CO or arsenic, and catalysts for CO oxidation or destruction of polychlorinated dibenzodioxins or dibenzofurans (PCDDs/PCDFs)[2,7-12]. All the group VIII elements show considerable activity for this process [13]. Among them Co, Fe and Ru present the highest activity [14]. Due to high activity for Fischer–Tropsch synthesis, high selectivity to linear products, more stability towards deactivation, low activity towards water-gas shift (WGS) reaction and low cost compared to Ru, cobalt-based catalysts are the preferred catalyst for Fischer-Tropsch synthesis [15,16]. In order to enhance the catalytic activity and stability, different combinations of these active metals have been reported such as Co-Fe [17], Co-Mn [18] and Fe-Mn [19]. The Fischer–Tropsch (FT) synthesis has long been recognized as a heterogeneous surface catalyzed polymerization process [20, 21]. Among the reported Fischer–Tropsch synthesis catalysts, iron and cobalt are used commercially at temperatures between 200 and 300 °C, and at 10–60 bar pressure [22–24]. The performance of these catalysts is affected by numerous factors, one of which is the nature and structure of the support materials. Most studies on FT catalysts have been performed with the metals supported on silica, alumina or titania [25]. Early comparative studies have revealed selectivities for olefin formation in the Fischer–Tropsch synthesis to be Fe/C > Fe/silica > Fe/alumina [26].

A novel process for the preparation of carbon based structured materials with controlled topology, morphology and functionality is discussed. The nanostructured materials are prepared by controlled reaction of fine-dispersed Al flakes with dichloroethane in paraffin medium in the presence of iron and cobalt chlorides. Compositional control over the system provides control over the structure of the phase separated precursor whose organization therein dictates the nanostructure of the material obtained during the process, where in each dimension of the formed structure can be predetermined. When the composition of the first nanostructured morphology is selected to comprise a continuous precursor matrix then a continuous carbon based nanostructured material is formed. The carbon and carbon based structures can find application in different areas, including petroleum chemistry, catalysis. Here in our paper we discussed the introduction of metals in the catalytic complex CTC with the direct participation of the metal salts in the reaction, resulting in formation of bimetallic complexes of the type Fe/CTC, and Co/CTC. Studies of the formation of metal-carbon structures of various dimensions are extremely important, because having these results, it is possible to develop a directed synthesis methods of metal-carbon structures required composition. The presence of nanostructured carbon and CTC modified with metal chlorides are confirmed by different techniques, such as X-ray fluorescence microscopy (XRFM), thermal analyses (TG/DSC), X-ray diffractometer (XRD), and Dynamic light scattering analyses for particle size determination.

## 2. EXPERIMENTAL

### 2.1 Chemicals

1,2-dichloroethane( $C_2H_4Cl_2$ ), 99.5% Sigma-Aldrich; Aluminium flakes, 99.99% Aldrich; Heptane ( $C_7H_{16}$ ), 99% Aldrich; Anhydrous Aluminium chloride( $AlCl_3$ ), 99% Sigma-Aldrich; ammonia solution, Iron (III) chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ), 99% Sigma-Aldrich; Cobalt (II) chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ ), 99% Sigma-Aldrich, analytical grade product were purchased and used as received.

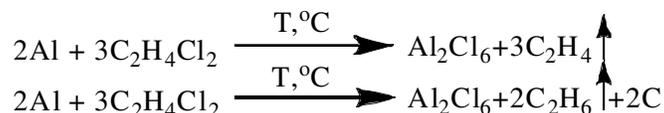
### 2.2 Synthesis of the Alumina Matrices Containing Fe III Ions and Co II Ions

The alumina matrices containing Fe III ions and Co II materials were synthesized as a catalytic complex CTC and CTC modified with metal chloride of Fe (III) and Co (II) [27] in laboratory conditions under atmospheric pressure in a solvent in the mode of «in situ», at a certain ratio of initial components in a round bottom flask (reflux system) at 80-90 °C for 22-25h. The obtained gel was cooled and aged in the mother liquor at room temperature for 24 h. After that, the solvent was removed under vacuum, and a final drying was carried out at 100-110 °C. The obtained dried xerogels (designated as

CTC-110, Fe/CTC-110, Co/CTC-110) was submitted to thermal treatment at 400, 600, and 850 °C for 2h in air, furnishing the materials designated as following:

complexes	200 °C	400 °C	600 °C	850 °C
CTC	CTC - 200	CTC- 400	CTC- 600	CTC- 850
Fe/CTC	Fe/CTC- 200	Fe/CTC- 400	Fe/CTC- 600	Fe/CTC- 850
Co/CTC	Co/CTC- 200	Co/CTC- 400	Co/CTC- 600	Co/CTC- 850

Under laboratory conditions, has been synthesized catalyst depending on the interaction of aluminum with dichloroethane in a solvent as following equation



### 2.3 Characterization Techniques

#### 2.3.1 X-ray fluorescence microscopy (XRFM)

Elemental analysis of the samples were performed by using X-ray microscope XGT-7000, Horiba with accelerating voltage of X-ray tube 50KV, the diameter of the incident X-ray beam was 100 microns, and the measurement time was 200 sec. the samples were crushed to powder and pressed. The Full Vacuum mode was used which provides elemental analysis for light elements such as aluminium, with the sample chamber maintained at normal atmospheric pressure.

#### 2.3.2 Thermal analyses

A Thermal Analyst “STA 449 F3 Jupiter” TG-DTA/DSC analyzer was used. For TG/DSC measurements, a covered corundum pan with samples weighting  $10.0 \pm 0.1$  mg was used. Data recorded upon heating up to 600 °C with heating rate of 10 K/min in a stream (40 ml/min) of nitrogen gas.

#### 2.3.3 Dynamic light scattering Particle Size Analyses (DLS)

The DLS analyses were carried out by the dynamic light scattering particle size analyzer LB-550 Horiba. The particle size measurements were conducted at a fixed 90° angle and a wavelength of 635 nm. The samples were measured at 25 °C which was chosen as this temperature is commonly used for DLS analysis, and 1, 2-dichloroethane was used as a dispersant solvent. To maximize the accuracy of the measurement, the samples were diluted before the DLS analysis by using the solvent mentioned above.

#### 2.3.4 X-ray diffractometer (XRD)

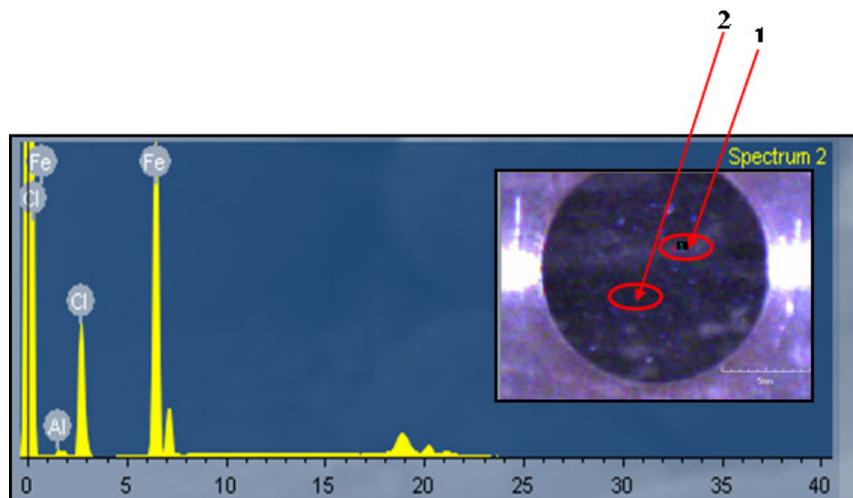
XRD patterns were obtained using TD-3500 diffractometer at room temperature. Diffraction patterns were obtained with none-filtered Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm), monochromatic X-ray beam, and X-ray tube parameters with 35 kv and 25 mA.

## 3. RESULTS AND DISCUSSION

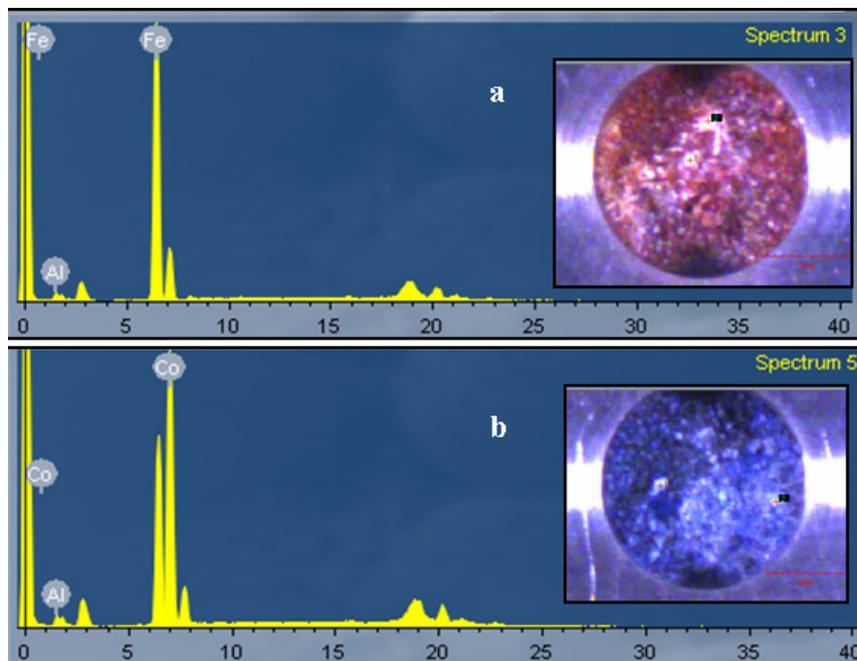
### 3.1 X-ray Fluorescence Microscopy (XRFM) Characterization

After heat treatment of these samples at 110 °C, it had been shown (Table 1, 2) that the distribution and mass thickness of aluminium, chloride, iron and cobalt elements, respectively, on the surface and over the depth at different positions is rather homogenous throughout the organism (Fig 1). And at 200 °C the mass thickness of chloride increases in case of aluminium catalytic complex and catalytic complex modified with iron due to the formation of dimmers Al<sub>2</sub>Cl<sub>6</sub> and Fe<sub>2</sub>Cl<sub>6</sub>, respectively which increasingly dissociates into the monomeric at higher temperature, in competition with its reversible decomposition to give metal (II) chloride and chlorine gas[28]. But in the case of the catalytic complex CTC modified with cobalt the mass thickness of chloride decreases, because the CoCl<sub>2</sub> is un reactive toward Cl<sub>2</sub>, and the dimmer can't be formed. The

stability of Co (III) in solution is considerably increased in the presence of ligands of greater Lewis basicity than chloride, such as amines. For samples after calcinations at 400 °C the distribution and mass thickness of chloride decreased due to the decomposition of Cl. Reports on decomposition of nickel chlorides were given by others [29] and stated that decomposition characteristics depend on initial ingredient. For the complex CTC modified with Fe the red ferric oxide mixed with black ferrous oxide were formed, and the complex modified with Co the grayish cobalt(II)oxide mixed with cobalt blue, cobalt (II) aluminate ( $\text{CoAl}_2\text{O}_4$ ) [30] were appeared as shown in Fig 2. Table 1, 2 showed the distributions of the percentages of aluminium, chloride, iron and cobalt elements, respectively. For CTC complex as prepared at 110 °C in air showed the percentages ratios of Al: Cl as 1:3 exists as  $\text{AlCl}_3$  and from the percentages ratios of Al: Cl: Fe the Fe/CTC -110 complex exists as  $\text{AlFe}_{1.4}\text{Cl}_{1.6}$ , the Co/CTC -110 exists as  $\text{AlCo}_{1.4}\text{Cl}_{3.02}$ . After the thermal treatment of the complexes at 200 °C, CTC complex exists as  $\text{AlCl}_{1.2}$ , the Fe/CTC-200 complex exists as  $\text{AlFe}_{2.08}\text{Cl}_2$ ; the Co/CTC -110 exists as  $\text{Al}_{1.2}\text{Co}_{1.3}\text{Cl}$ .



**FIGURE 1:** EDRF analysis and optical image of initial CTC-200 at (1) light and (2) dark points



**FIGURE 2:** EDRF analysis and optical image of (a) Fe/CTC-600 (b) Co/CTC-600 complexes

**Table 1:** The Content of elements (wt. %) in samples treated at 110, 200 °C for 6 hours and their distribution over the depth at light points

Samples name	Elements (wt. %)				The distribution of elements over the depth			
	Al	Cl	*C	Fe	Al	Cl	Fe	Co
CTC-110 Fe/CTC-110 Co/CTC-110	19.7	59.2	21	-	0.035	0.142	-	-
	19.7	31.7	21	27.6	0.045	0.178	0.255	-
	15	45.4	18.4	-	0.031	0.214	-	0.305
CTC-200 Fe/CTC-200 Co/CTC-200	35	42.7	22.2	-	0.062	0.082	-	-
	15.8	30.2	21	33	0.332	0.498	0.406	-
	27.4	22.5	20.7	-	0.113	0.118	-	0.194

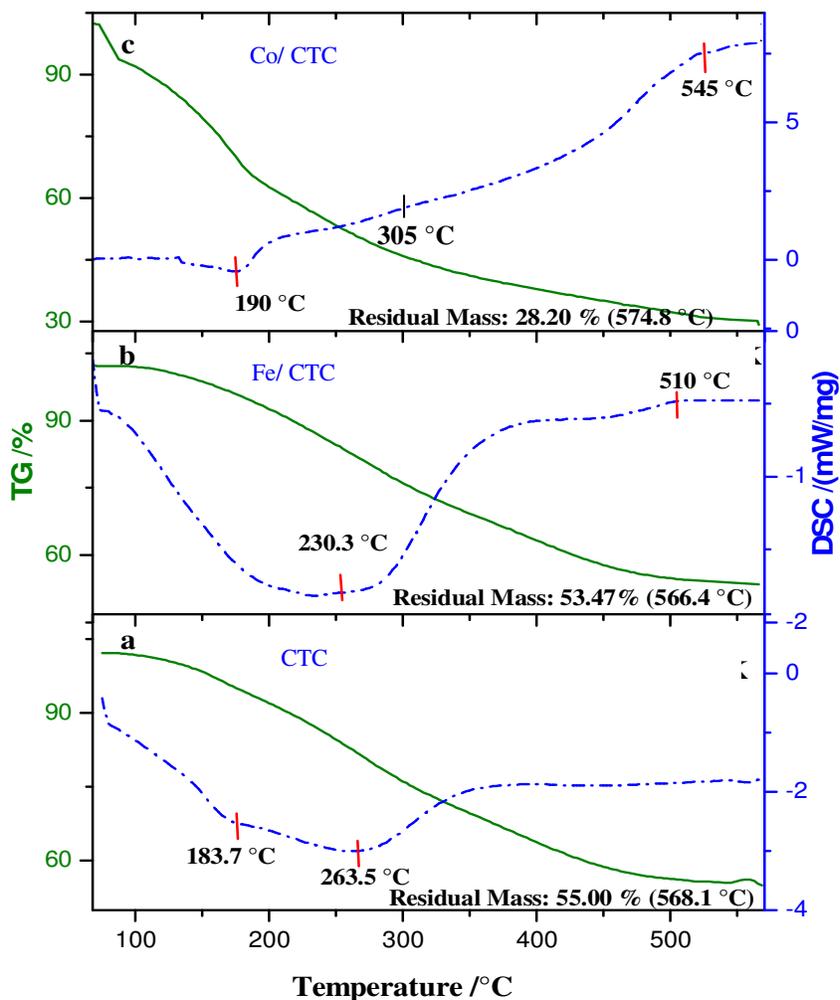
**TABLE 2:** The Content of elements (wt. %) in samples treated at 110, 200 °C for 6 hours and their distribution over the depth at dark points

Samples name	Elements (wt. %)				The distribution of elements over the depth			
	Al	Cl	*C	Fe	Al	Cl	Fe	Co
CTC-110 Fe/CTC-110 Co/CTC-110	17.3	61.6	21	-	0.028	0.142	-	-
	17.3	33.5	21	28.1	0.048	0.236	0.316	-
	14.9	45.6	18.4	-	0.030	0.217	-	0.303
CTC-200 Fe/CTC-200 Co/CTC-200	34.04	43.6	22.2	-	0.077	0.117	-	-
	15.9	30.8	21	32.3	0.325	0.504	0.399	-
	26.9	23.2	20.7	-	0.106	0.120	-	0.184

\* C content was determined by the balance of the treatment of the samples at 110,200 °C.

### 3.2 Thermal Analyses Characterization

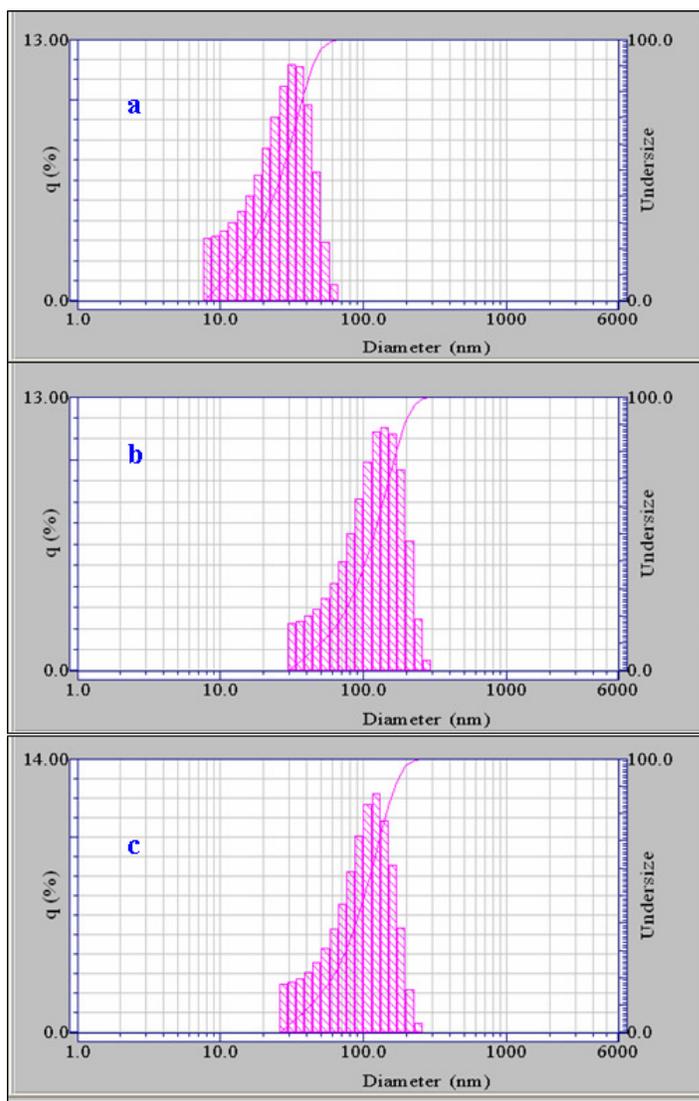
Figure. 3 shows the TG curves for the materials of CTC and modified with iron and cobalt chlorides at 110 °C, results showed that the evolution of composite materials occurred through a three step process, It is seen that the first step for the total water loss was equal to 4% (for CTC), 6.3% (for Fe/CTC) and 9.2% (for Co/CTC) revealed that maximum water loss found at 190 °C which can be linked to the loss of water of crystallization which accompanied with a small endothermic in DSC curve were clearly observed at 183 °C for AlCl<sub>3</sub>, 230 -250 °C for partial decomposition of FeCl<sub>3</sub> to FeCl<sub>2</sub>+ Cl<sub>2</sub>, and at 190 °C for CoCl<sub>2</sub>. The second step the residual mass was 18% at 263 °C (for CTC), 12% at 230 °C (for Fe/CTC) 45.34% at 305 °C (for Co/CTC) respectively, is probably may be due to the collapse of the aluminum compounds and the inorganic complexes with the simultaneous processes of sublimation of some of these compounds and the evaporation of the chlorides and solvent residue. The final step the residual mass was 45% for CTC at 568.1 °C, 46.5% for Fe/CTC at 566.4 °C and for Co/CTC was 71.8% at 574.8 °C. The increase of weight loss for these complexes may be attributed to the introduction of iron and cobalt chlorides in the carbon matrix. These weight loss followed by an exothermic one at 510 °C for Fe/CTC and another at 545 °C for Co/CTC sample, this because in N<sub>2</sub> atmosphere (absence of O<sub>2</sub>) the decomposition/composition processes of the precursor materials may produce incomplete oxidation products such as CO gas and carbon materials.



**FIGURE 3:** TG and DSC curves of the precursor materials (a) CTC (b) Fe/CTC (c) Co/CTC in flow of N<sub>2</sub> gas.

### 3.3 Dynamic light Scattering Particle Size Analyses (DLS) Characterization

The method of DLS has been established that, all samples showed a non-symmetric distribution mean, median and mode are of three different values (Table 3). The catalytic complex CTC shows a comparison of the aggregation and impurities observed for the modified systems with metal chloride at 110 °C due to the addition of transition metals in the system which increases the size of particles and increases the degree of the aggregation. Figure 4 shows the different particle size distributions and different average particle size values of the catalytic complexes CTC, Fe /CTC and the Co/CTC depending on the composition.



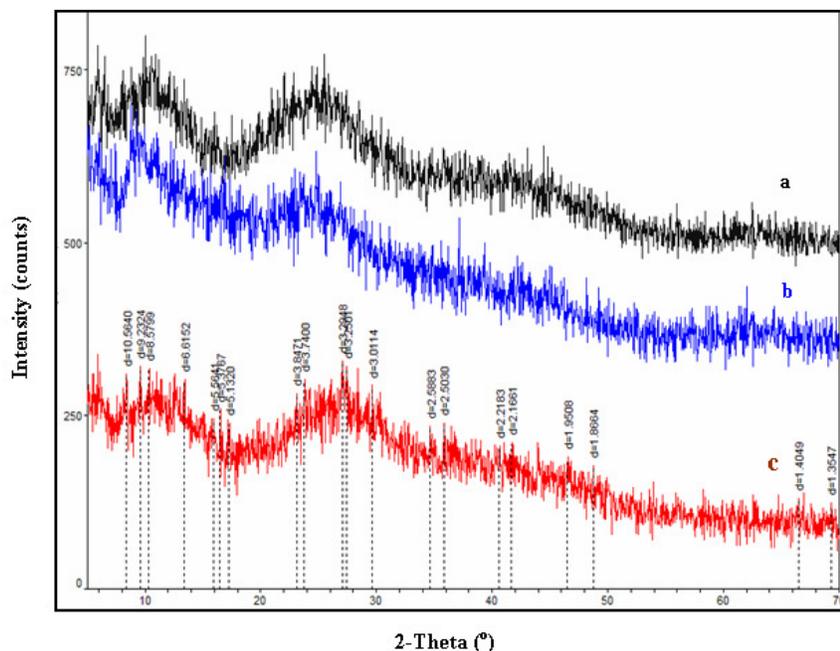
**FIGURE 4:** DLS spectra of precursor samples at 110 °C (a) CTC (b) Fe/CTC(c) Co/CTC

### 3.4 X-ray Diffractometer (XRD) Characterization

Wide angle XRD, WAXRD patterns for the catalytic complexes CTC, Fe/CTC and Co/CTC obtained with heat treatment at 110 °C are shown in Fig. 5, small angle XRD, SAXRD patterns of the same set of materials are inserted. The patterns showed that we have an amorphous structure for our systems also the d-spacing values in the small angle range is larger than that of the lattice planes that is means that these materials exist as aggregates of particles which is conformed with DLS analysis.

**TABLE 3:** The particle size distributions and average particle size values of the desired catalytic complexes

Samples name	Diameter on 10%	Diameter on 50%	Diameter on 90%
CTC-110	11.5	27	44.4
Fe/CTC-110	50.5	118.3	194.5
Co/CTC-110	42.7	101.4	166.7


**FIGURE 5:** XRD patterns of precursor samples at 110 °C (a) CTC (b) Fe/CTC (c) Co/CTC

#### 4. CONCLUSIONS

This work simplifies established a novel process for the preparation of carbon based structured materials process of modifying of the catalytic complex CTC with the chlorides of iron and cobalt metals under different calcined temperatures and characterized with different techniques. Here in our paper we discussed the introduction of metals in the catalytic complex CTC with the direct participation of the metal salts in the reaction, resulting in formation of bimetallic complexes of the type Fe/CTC, and Co/CTC. The XRD and DLS results showed that, the materials formed without calcinations were noncrystalline, and exist as aggregates, and the DLS analysis is very sensitive to aggregation and large impurities, even at low concentrations. TG analysis showed that the precursor complexes were thermally stable, and its thermal degradation occurred through a three step process. XRFM characterization showed that our system of high homogeneous elemental distribution on the surface and overall the sub layer surface, and after calcinations of the targeted catalytic complexes at different calcined temperatures have different phases of iron and cobalt aluminates.

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