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X-ray Analysis for Purification Process of Synthesized Multi-Walled Carbon Nanotubes by Chemical Vapor Deposition

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ABSTRACT: In this work we report method that can be used for the purification of multiwall carbon nanotubes (MWNT) obtained by the CVD chemical vapor deposition method. The purification of multiwall carbon nanotubes are required in order to eliminate by-product that represent by the metal catalyst and unconverted carbon such as amorphous carbon. The purification of the sample was carried out by treatment with three steps ultrasonic water bath and separation funnel with ethanol, hydrogen peroxide, and then reflux with nitric acid. Later, we have reported method for purification synthesized MWNTs by reflux with nitric acid only to show the effect of the first two steps. The results show that treatment the sample with three steps were succeed to increase the purities of carbon nanotubes more than the method that depend on reflux. The samples were analyzed using, powder X-Ray diffraction (XRD) and measuring surface area. The results has discussed as compare with standard MWNTs from Aldrich.

Keywords: multi-walled carbon nanotubes, separation funnel, x-ray, particle size

I. INTRODUCTION

The most important nanostructures of carbon material are carbon nanotubes (CNTs). The molecular structure of carbon nanotubes consists of pristine carbon atoms linked together to look like polymer in a hexagonal arrangement with monolayer of carbon atoms [1-2]. The new carbon-material appear to become a reality for science thanks to Iijima [3], who synthesized one type of carbon nanotube called a single wall SWNT in 1991 with Ichihashi [4]. This was a challenge and temptation at the same time due to its physiochemical properties [5] being unknown to some extent, and the variety of types of single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs), few-walled carbon nanotubes (FWNTs), and multi-walled carbon nanotubes (MWNTs). Extensive studies and research were done on these materials due to many specific physiochemical properties and representing the most abundant element in nature. Generally, there are three primary methods which are used for the synthesis of carbon nanotubes; Chemical Vapor Deposition (CVD) [6], Arc-Discharge [7], and Laser Ablation [8]. In recent years, carbon nanotubes have been prepared under different labels for the various techniques, in fact represent the development of methods and techniques for the three methods mentioned above, with new titles [9-10]. The rise of unique properties of carbon nanotubes mostly depends and influenced by the purities of product in the sample whenever the ratio was the highest efficiency of product should be more purity. The as-prepared carbon nanotubes usually contain amount of byproduct which represent by unconverted carbon such amorphous carbon, and multi-shell carbon nanocapsules in addition to impurities from catalyst and support particles [11]. The impurity is serious impediment to characterization of the properties nanotubes due to interference the impurities and carbon nanotubes. For this, many ways has been developed in order to increase the purity of the product by using many techniques which can be given an acceptable result for the researcher.

Hou, *et al.* [12] reported that a simple procedure for the purification of the single-walled carbon nanotubes which include three steps ultrasonic in alcohol, and oxidation in fixed air, then soaking in hydrochloric acid. The measurement of Thermogravimetric analysis shows that 41 wt% purity of yield SWNTs was achieved after purification.

Park *et al.* reported that [13] Multi walled carbon nanotubes were synthesized by electric arc discharge method in helium ambient with the pressure of 400 torr then the thermal annealing were used for purified the product. The quartz tube was rotated during the annealing of product in air which depend to increase the activity to remove the carbonaceous which rise to about 40% of MWNTs. Ngo *et al.* published [14] that the purity of carbon nanotubes (CNTs) was evaluated by using a X-ray difraction, Raman spectroscopy, Thermogravimetric analysis and energy dispersive X-ray fluorescence spectroscopy. The purity of the CNT samples was found to be greatly increased when annealed in air or in vacuum. Hou *et al.* [11] reported that purification procedure Multi-walled carbon nanotubes can be done by ultra-sonication, heat treatment in hot water, bromination, oxidation and acid treatment. The procedure that produces MWNTs with purity could approach 50% which detected by thermogravimetric analysis and transmission electron microscopy. The common techniques that used for purification were include oxidation with, hydrochloric acid, make activating with organic materials, filtration, mechanical purification, chromatography techniques, and microwave heating methods [15]. In the same time the process of remove the impurities cause a significant amount of CNTs is destroyed during purification processes [16]. The XRD analysis rarely reported to identify the process of purification for synthesized carbon nanotubes while TGA, Raman spectroscopy, with XRD commonly sue for this purpose. In this paper, we report a simple method that appears to be quite suitable for the purification of MWNTs synthesized by the chemical vapor deposition method without catalyst. The XRD analyses were used in this study to distinguish the change in practical size of synthesized MWNTs. The purification procedure includes using water bath ultrasonic with separation funnel, oxidation in hydrogen peroxide, then by reflexes with 5% of nitric acid.

II. EXPERIMENTAL

A. Materials

The material used in this experiment was Ethanol (99.93%) from Alfa, Aesar and Methanol (99.85%) from Hyman, England, 1-butanol with a purity of 99.5% was supplied by Merck. All of alcohols were used without further purification. The HNO_3 received from Fisher Chemicals with concentration 70% and density 1.42 g/cm^3. Hydrogen peroxide H_2O_2 was purchase from Barcelona, Spain in 30% percent weight. The N_2 gas used in purities 99.999% from Emirates industrial gases. The standard MWNTs, used in this study with purity 95% and mode diameter 5.5 nm were purchased from Aldrich. According to the product specifications, the compound was fabricated by chemical vapor deposition method.

B. Synthesis of MWNTs

Multi walled carbon nanotubes were prepared by chemical vapor deposition method CVDs with using Tube furnaces, made from XIN YOO electronic components co. Ltd. from chains. The mixture of (1:1) methanol and Butanol use a source of carbon. The boat of silica were selected as support for precipitation. The typical reaction of precipitate was made at 750°C for 30 min in a nitrogen atmosphere with flow 125 cm^3/min. After deposition, the furnace was switched off and allowed to cool down to room temperature under a continuous N_2 flow, then the product was collected for purification before the characterizations process.

C. Purification Process of MWNTs

Multiwall carbon nanotubes were purified by applying two different ways. One method was used to purify multiwall carbon nanotubes by reflux with 5%HNO_3 directly, while the second include mechanical treatment and oxidant with H_2O_2 before the reflex with 5%HNO_3. Briefly the process explains in Fig. 1.

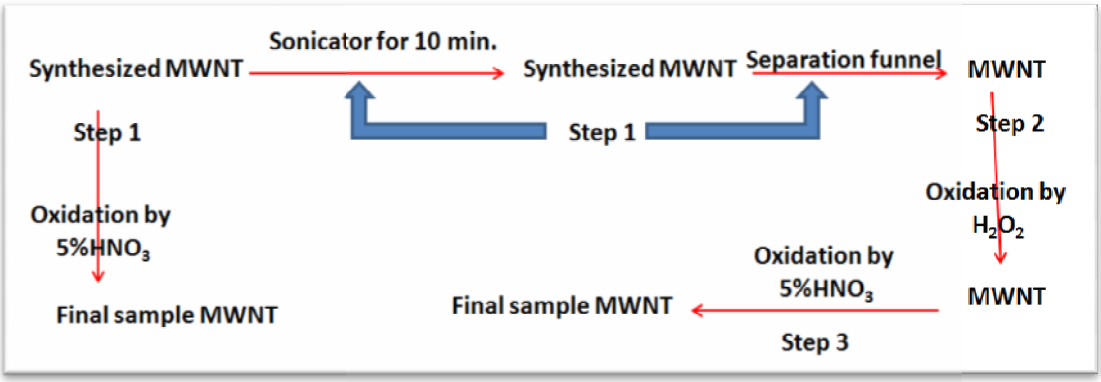

Fig. 1. Schematic of purification process for synthesized MWNTs.

The first step consists of (125 mg) from the sample were dispersed with ultrasonic water bath in 150 ethanol alcohol for 10 min. The complementary of first step include using separation funnel, to re-distribution the aggregates particles which, will be removed from solution then complete the oxidation as shown in Fig. 2. The second step were oxidized the product from first step with H_2O_2 at 15°C for 12h. After that, the solution allowed to reach for room temperature then heated gradually to 80°C for 5h. The third step completes the oxidation of product when the black product was reflux with 5% HNO_3 at 80°C for 5h. Finally, the sample was washed with deionized water and dried at 100 °C for 12h.

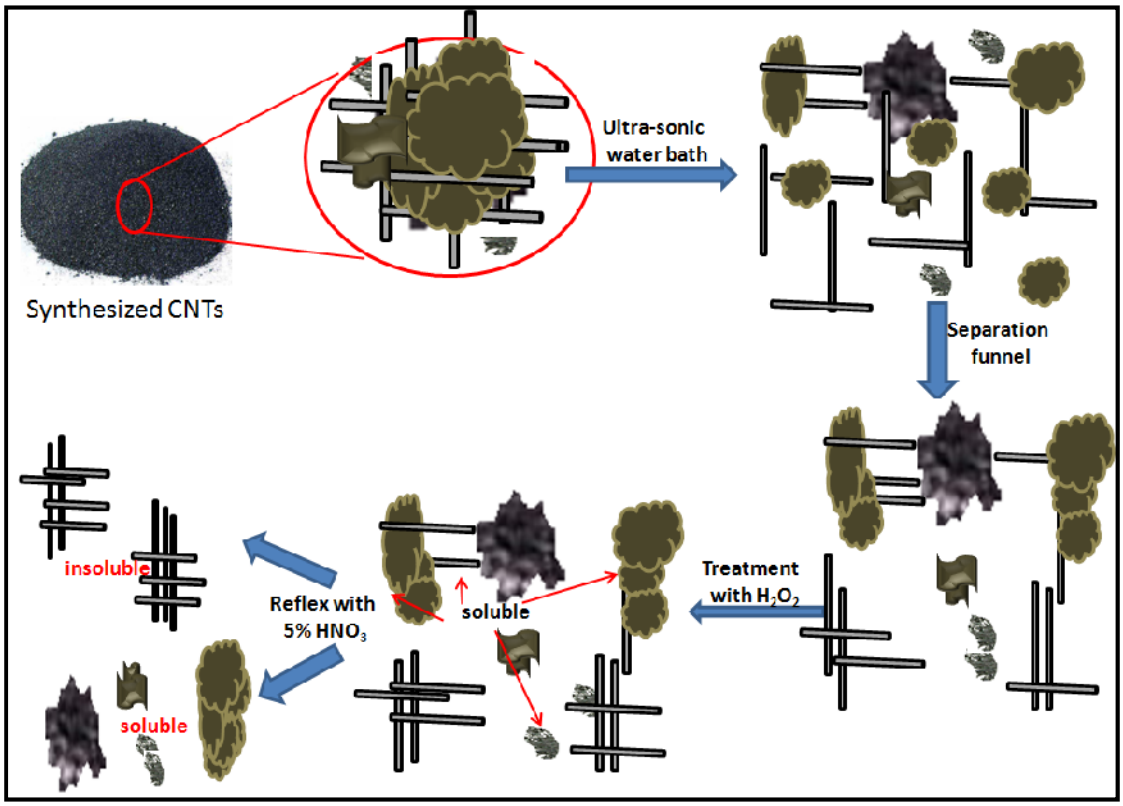

Fig. 2. Schematic diagram for the dispersion and re-distribution the sample of as grown MWNTs.

III. CHARACTERIZATION

X-ray diffraction was performed in order to determine the purities of MWNTs by modify method. The process includes three steps: chemical oxidation materials and mechanical process that depend to remove most the impurities. The X-ray diffraction (XRD) patterns were done on a (Rigaku Rotalflex) (RU-200B) X-ray diffractometer using Cu Kα radiation (wavelength 0.15405 nm) with an Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ angular regions between 10 and 80° were explored at a scan rate of 5°/min. For all the XRD analysis, the resolution in the 2θ scans was kept at 0.02°. The BET surface area was measured by using Micromertics Auto MATE 23. The process includes heating the sample in specific tub at 120°C than contact the tube to the system which immersed the tube in nitrogen liquid to complete the measurement. Fig. 3 represent the standard MWNTs from Aldrich which uses to compare with synthesized MWNTs in different steps of purification. Fig. 4 shows as grown MWNTs powder without any purification from CVDs method by using methanol/1-Butanol (1/1) as source of carbon. Fig. 5 refer to MWNTs after treated with ethanol (Synthesized MWNT+ROH) with the assistance of sonicator water bath. Figure 6 include XRD analysis of the sample which treated with ethanol than with H_2O_2 (Synthesized MWNT + ROH + H_2O_2). Fig. 7 shows the sample which produces from step 2 than treated with 5% HNO_3 (Synthesized MWNT + ROH + H_2O_2 + HNO_3). Figure 8 refer to the as-grown MWNTs which treated directly with 5% HNO_3 without ROH and H_2O_2. The X-ray diffraction patterns were used to determine the crystallite size (d) estimation by line broadening measurements at ≈ 25 in the Debye-Scherrer equation [17]:

$$d = K \lambda / \beta \cos\theta$$

Where *d* is the average crystallite size (nm), λ is the X-ray wavelength in nanometers (nm) equal to (0.15405 nm), β is the peak width of the diffraction peak profile at half the maximum height resulting from small crystallite size in radians, and K is a constant related to the crystallite shape mostly equal to 0.9. Fig. 3 shows MWNTs from Aldrich had two characteristic peaks at 2° = 25.5° and 43.3° [18] can be attributed to the diffraction from the C(100) and C(002) planes of the carbon nanotubes. The XRD patterns for all the samples in three steps of purifications and as grown MWNTs shows variance in quantities and qualities for the standard peaks of material.

From figure 4 for as grown MWNTs without purification obviously seen that impurities make the first standard peaks shift and reduces in intensity in addition to disappear the second standard peaks [19]. The MWNTs as grow shows peaks with high intensity at 14.25°, 17.20°and 18.51°due to many crystal structure mostly related to SiO_2 [20]. The impurity shows very high intensity are remove or at least reduces the peaks of MWNTs in the xrd pattern. The first steps of purification which include using ethanol to dispersion the MWNTs by sonicator water bath than use separation funnel to re-distribution the materials in mixture. The results of process shown in figure 5 which related to exist two standard peaks at 25.09° and 43.44°. The peaks at 29.5° can be related to remaining of graphite [21] which produces during the precipitation. When using H2O2 as oxidant agent the first peaks 25.33° shows change when shifting to +0.21° while the second peak 43.42 ? did not change clearer as shown in figure 6. The third step treatment with 5% HNO_3 casing large shift about +1.13 when appears at 26.26° while the second peak witness very small shift with 43.40° as shown in Fig. 7. The last sample was taken to study the importance of steps that preceded the treatment with acid when the sample treated with 5%HNO_3 only as shown in Figure 8. Mostly materials that con be remove in the first part of purification which related to heavy organic material, unconverted carbon and amorphous carbon [22].

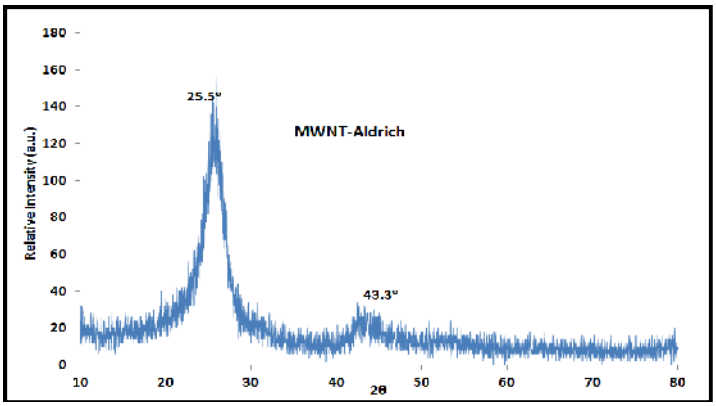

Fig. 3. XRD patterns of standard MWNTs from Aldrich.

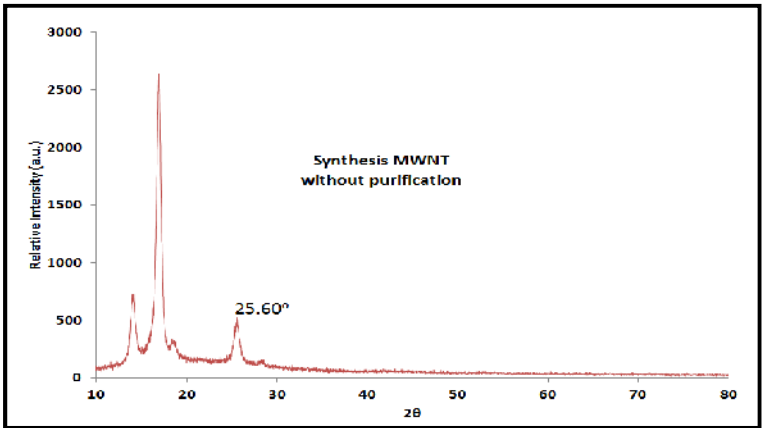

Fig. 4. XRD patterns of as grown MWNTs by chemical vapour deposition from mixture Methanol:Butanol (1:1) at 750°.

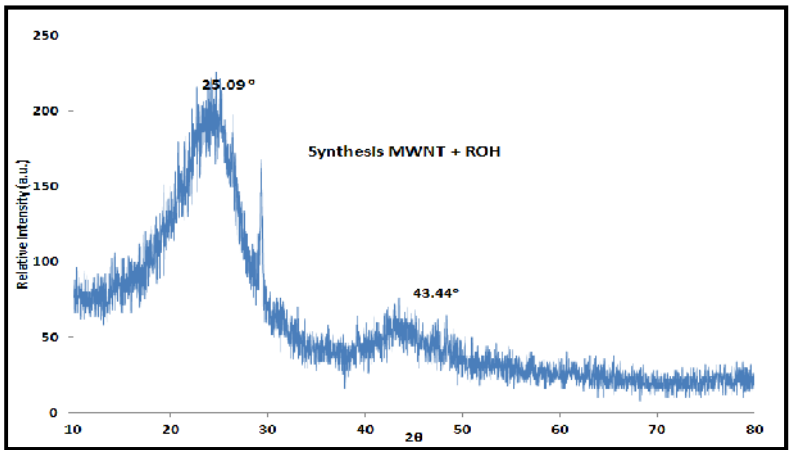

Fig. 5. XRD patterns of synthesized MWNTs after treatment with ethanol in exist of ultra-sonic water bath.

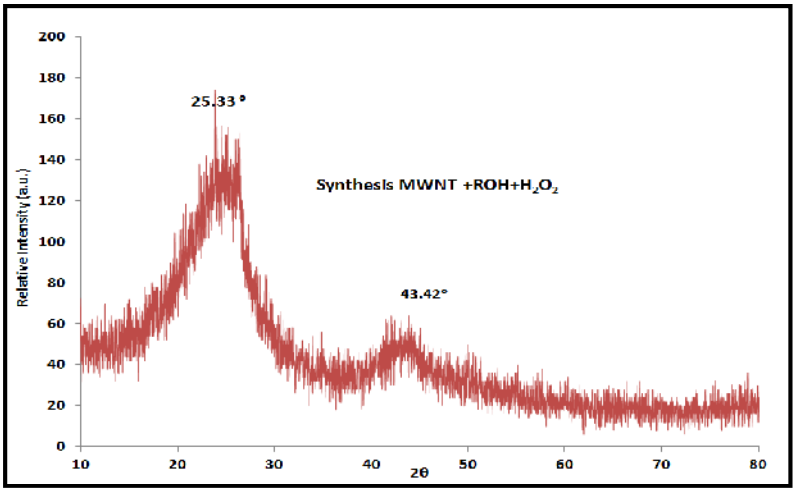

Fig. 6. XRD patterns of synthesized MWNTs after treatment with ethanol in exist of ultra-sonic water bath than with H_2O_2.

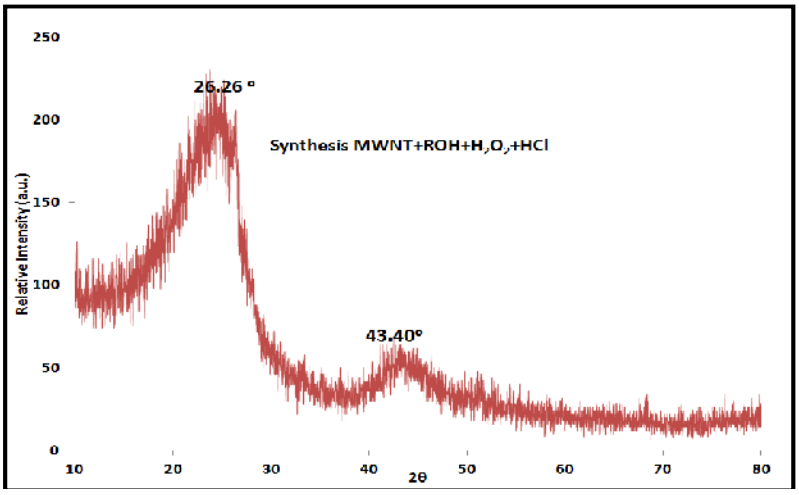

Fig. 7. XRD patterns of synthesized MWNTs after treatment with three steps ethanol, H_2O_2 than with 5% HNO_3.

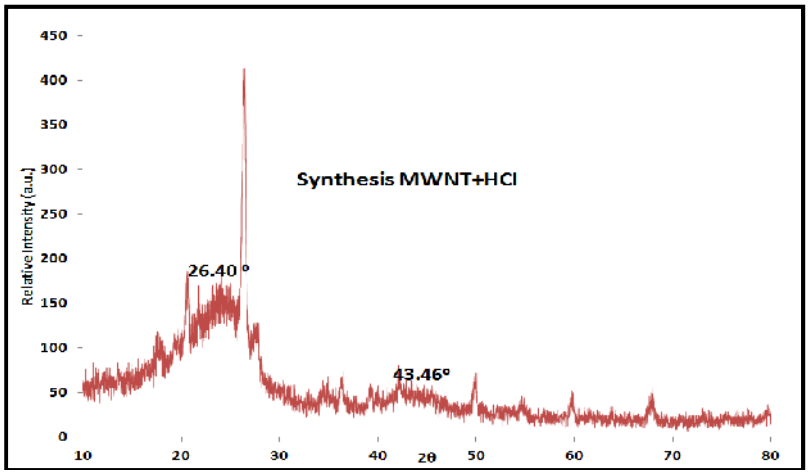

Fig. 8. XRD patterns of synthesized MWNTs after treatment with 5% HNO_3 only.

In spite of exist main peak at range 25° with positive or negative deviation, but the variance on calculus of particle size was change from sample to ether. The shift of peaks effect [23] with the ratios and types of impurities in the sample [24]. Table 1 show that samples with different condition of treatment refer to important three points of purification. The first is the reflux with nitric acid after treatment with ethanol than H_2O_2 did not change of crystalline in carbon nanotubes, but make change of the crystallite size of the nanopowders that agree with results of Stanch *et al.* [25]. The second point is the first two steps before reflex was very important to remove many impurities in the sample which enhance the activity of reflex. The third point related to particles which wittiness large size due to aggregate the groups when using direct reflex without mechanical treatment and oxidation with H_2O_2. The surface area which listed in Table1 shows that increase the surface area with increase the purities [26] of sample was change from 91 to 179 cm^2/g. the treatment with ethanol in first steps was succeeds in reaching for maximum surface area as compare with the anther steps. The last behavior could be related to nature of by-product during preparation without catalyst, mostly produces uncovered carbon that can be removing in the first step. The surface area for the sample with direct reflex confirms the result when reducing the surface area with increase the particle size in exist of impurities.

Table 1: Summary of characterized XRD peaks FWHM, particle size and surface area.

Sample	**2θ°**	**FWHM = β**	**D(nm)**	**S_{BET} (m^2/g)**
MWNT-aldrich	25.52	2.263	3.58	282
MWNT-as grown	25.60	0.696	11.65	91
MWNT-ROH	25.09	1.316	6.18	138
MWNT-ROH+ H_2O_2	25.33	1.109	7.73	151
MWNT-ROH+ H_2O_2 + HNO_3	26.26	1.162	7.00	179
MWNT + HNO_3	26.40	0.442	18.38	148

CONCLUSIONS

The purification process directly influence on the method of synthesis of carbon nanotubes and the condition of production. In this work a simple procedure to purify multiwall carbon nanotubes obtained by chemical vapour deposition method with using surface of silica as support for precipitation without catalyst. The remaining supports and unconverted carbon were removed by mechanical and chemical treatment.

The mechanical treatment succeeds in removing most of impurities which complete by using oxidant materials in tow steps. Oxidized by refluxing in 5%HNO_3 were shown more activity when used after two steps of purification as compare with the reflex without the two steps. The important of the first two steps not only to remove the impurities but also to prevent or at least reduces the agglomeration that could form in the reflux steps.

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