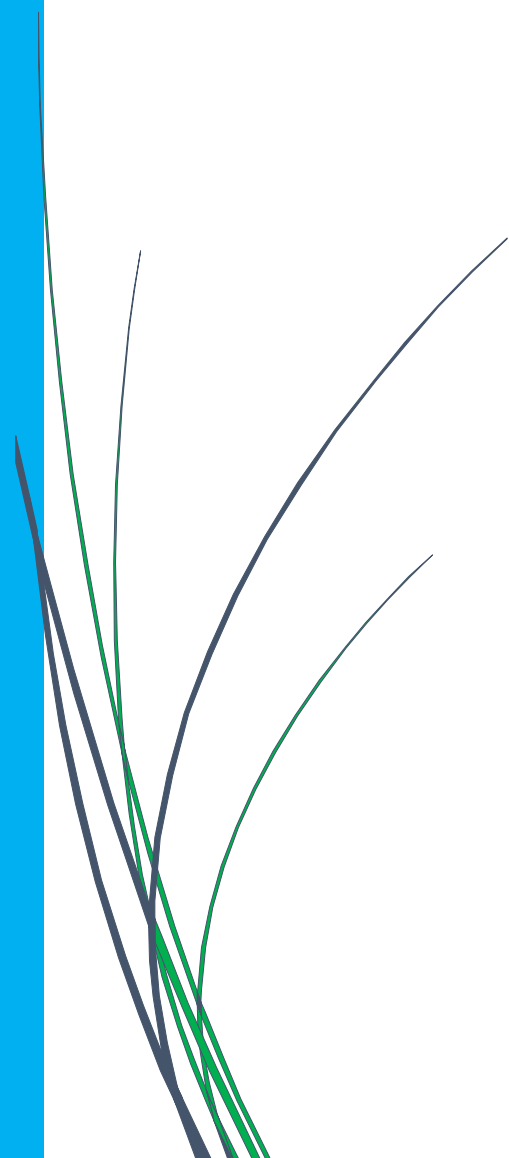


Chapter:4

Carbonaceous deactivation of Co catalyst after ESR



4.1 Introduction

Different phase stability and activity suggest that Co is not only highly active for ethanol steam reforming (ESR) in its metallic form, but also major contributor for carbon deposition [253, 254]. Co^{2+} and Co^0 states are active in acetaldehyde as well as in ethanol steam reforming [255, 256]. Yue et al. [257] suggested that addition of Co in the Ni metal catalyst alloy is able to reduce the carbon deposition during ESR. Among non-noble metal catalysts, Co-based catalyst with various supports were used by several authors for ESR process [39, 90, 105, 222, 258-263]. It reveals that cobalt is highly active for ESR especially at 753K. However, carbonaceous deposition is a significant issue regarding catalyst stability. Different cobalt precursors have also significant contribution in carbon deposition at catalyst surface. The effect of different precursors over carbon deposition was reported by Song et al. [264] with nitrate, chloride, sulfate, acetate, octacarbonyl, carbonate, acetyl acetate and oxalate but ESR performances were not reported with cobalt oxalate precursor. One objectionable point was that they used ethanol as an impregnation medium for each precursor to impregnate over CeO_2 . Because, the cobalt oxalate precursor is insoluble in ethanol and therefore it is not a good impregnation medium for aforementioned precursor. As cobalt oxalate is soluble in ammonia solution, it can be used as impregnated medium for better distribution of active metals.

The literature survey suggests that metallic cobalt phase is active for C-C bond scission but it also contributes for carbon filament formation [120, 123, 265]. The significant property of cobalt oxalate is that *in situ* thermal treatment in inert atmosphere at 673K typically forms cobalt metallic state [248]. In case of few supported Co-based catalysts need a promoter to be reduced completely in metallic phase [266]. Tuti et al. [267] studied ESR performance over bare Co metallic catalyst by pre-reducing Co_3O_4 . However, times on stream and carbon formation studies were not confirmed. The study

about filamentous carbon formation during ESR has not been thoroughly studied and is still under investigation. Few authors had suggested the tip growth phenomenon occurs during ESR, whereas, others contradicted this mechanism [72, 102, 112]. Therefore, the present study over baren active cobalt metal has been anticipated to provide new insight of this probable mechanism.

4.2. Experimental

4.2.1 Catalyst preparation

Analytical reagent grade cobalt (II) oxalate dihydrate ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) precursor was used for active Co-catalyst preparation. The cobalt metal catalyst was thermally prepared from $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor in inert atmosphere at 773K. The $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (5g) was kept in a tubular reactor and N_2 gas was continuously fed (40ml/min) to it. The temperature was increased at the rate of 10K/min up to 773K and annealed for 1h at the same temperature. Then, the catalyst bed was cooled in the same atmosphere up to room temperature and the formed Co metal was collected and stored in an air tight desiccator for further characterization and experimentation.

4.2.2 ESR Performance

ESR was performed at atmospheric pressure with cobalt catalyst (500mg) in a fixed bed flowed quartz tubular vertical reactor having length 40 cm and inner diameter of 3.2 cm. Ahead of reactor, the preheater was assembled to evaporate the ethanol and water mixture (molar ratio=3:1) fed with the help of syringe pump at the rate of 4ml/hr. The ESR was performed 573K-923K with 50K temperature interval. The time on stream performance was done at 723K reaction temperature, since it was found as a best

optimum temperature. After ESR performance, N₂ was flushed for 30 min to remove the ethanol-water mixture vaporized feed mixture.

4.3. Results and discussion

4.3.1 Characterization studies

4.3.1.2 Textural analysis

The surface area of Co metal was found to be 3.93 m²/g but after 21h of reaction, the surface area of cobalt with carbon increased to 108.12 m²/g. The pore volume was also found to be higher for cobalt with carbonaceous mixture. This is due to presence of nano carbon filament formed during ESR reaction.

Table 4.1 Surface area and pore volume of catalyst and spent catalyst.

Sample Catalyst	Surface area (m ² /g)	Pore volume (ml/g)
Co-catalyst	3.9	0.004
Co-catalyst + Carbon	108.1	0.160

4.3.1.3 XRD Analysis

The cubic-face-centered crystallites of Co peak at 2θ value 44.20°, 51.53° and 75.87° were matched with JCPDS (89-4307) with assigned plane (111), (200) and (220) respectively. Whereas, the 2θ value 36.47° (111), 42.4° (200), 61.47° (220), 73.62° (311) and 77.49° (222) were found corresponding to JCPDS (71-1178) of CoO. Moreover, the intensity of Co peaks of each planes were found to be greater than comparative to the peak intensity of CoO [Figure 4.1].

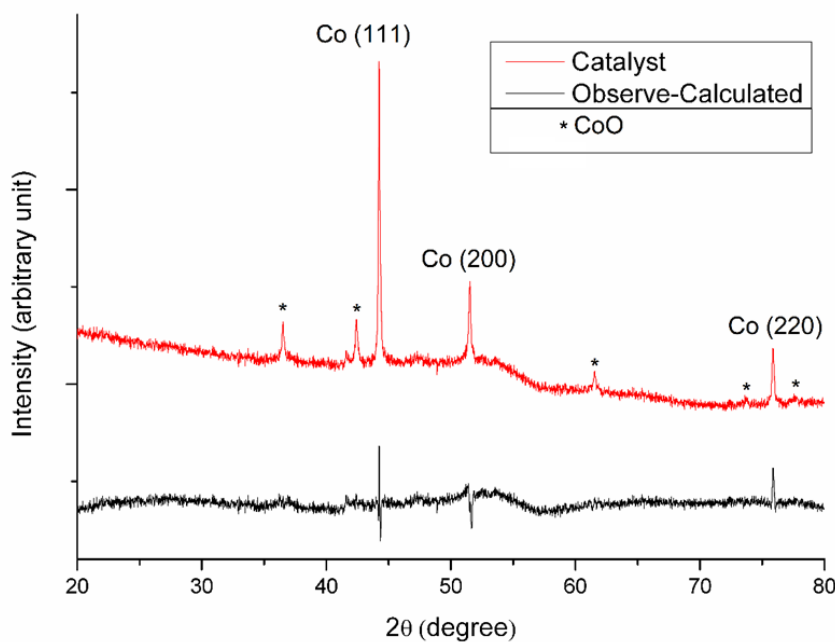


Figure 4.1 XRD pattern of Co catalyst with rietveld refinement.

The planes (111), (200) and (220) were observed to be common in both phases of Cobalt. The intensity of (111) plane was found highest as compared to other planes for Co^0 phase whereas, intensity of (111) and (200) planes are comparable to CoO state of cobalt. Overall, the (111) plane was predominantly formed on the cobalt catalyst. The Rietveld refinement was performed for both phases of cobalt. The *in-situ* formation of Co and CoO were also supported by the EDS analysis of catalyst as shown in Figure 4.2. It shows highly intense peaks of Co with less intense peaks of oxygen which indicates significant amount of Co^0 formation as compared to CoO . The unmarked peak in EDS graph was that of copper, because of the use of copper grid for sample preparation. The crystallite size calculated were found as 19nm, 22.34nm and 26.10nm respectively whereas, the particle size calculated with the help of image-J software was found in the range of 500-600 nm. The larger particle size suggests sintering due to *in-situ* thermal treatment process.

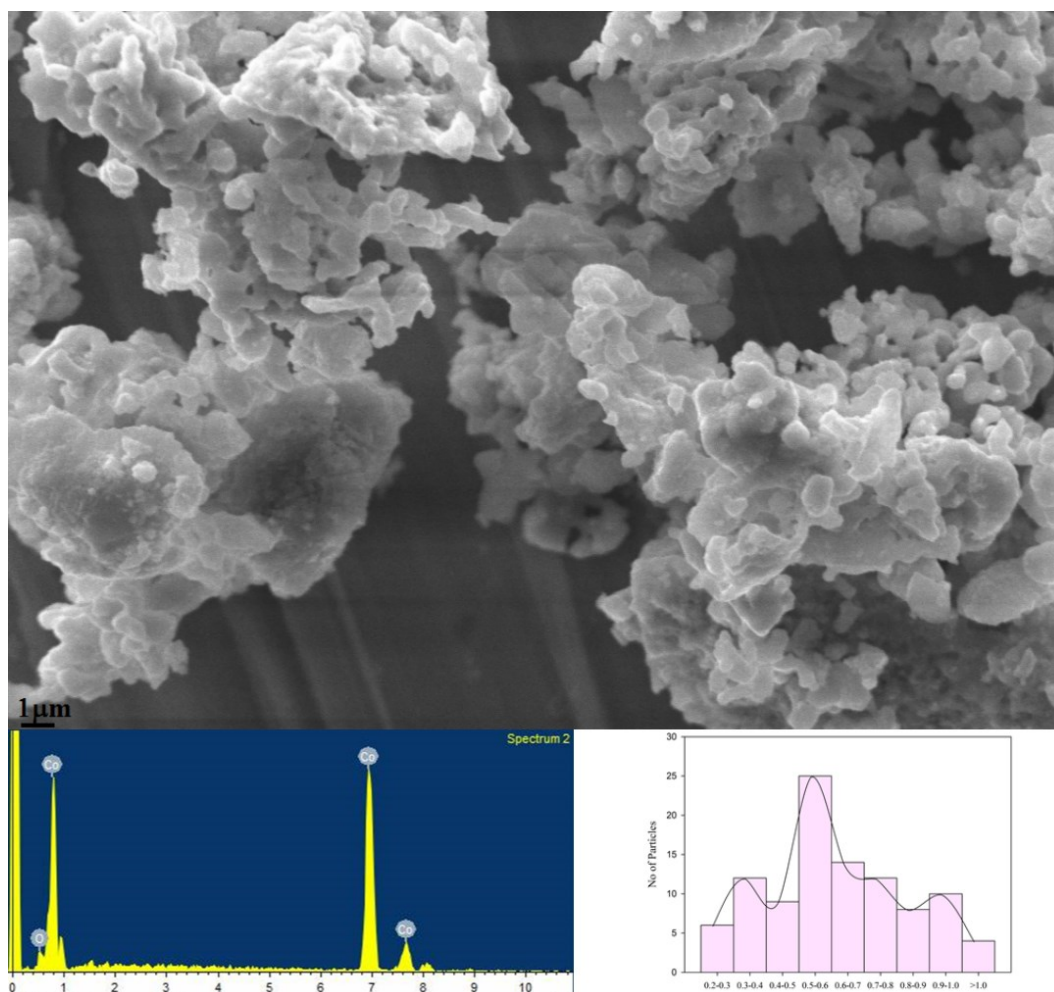


Figure 4.2 SEM image with EDS of Co catalyst.

4.3.2 ESR performance test

The selectivity of gaseous products generated and ethanol conversion during ESR were shown in Figure 4.3. The ethanol conversion was completed at temp 723K. The selectivity of H₂ and CO₂ was found highest at 723K. The CH₄ selectivity was reduced with increasing temperature whereas, CO selectivity was increasing at higher temperature. It might have occurred due to decomposition of ethanol at higher temperature.

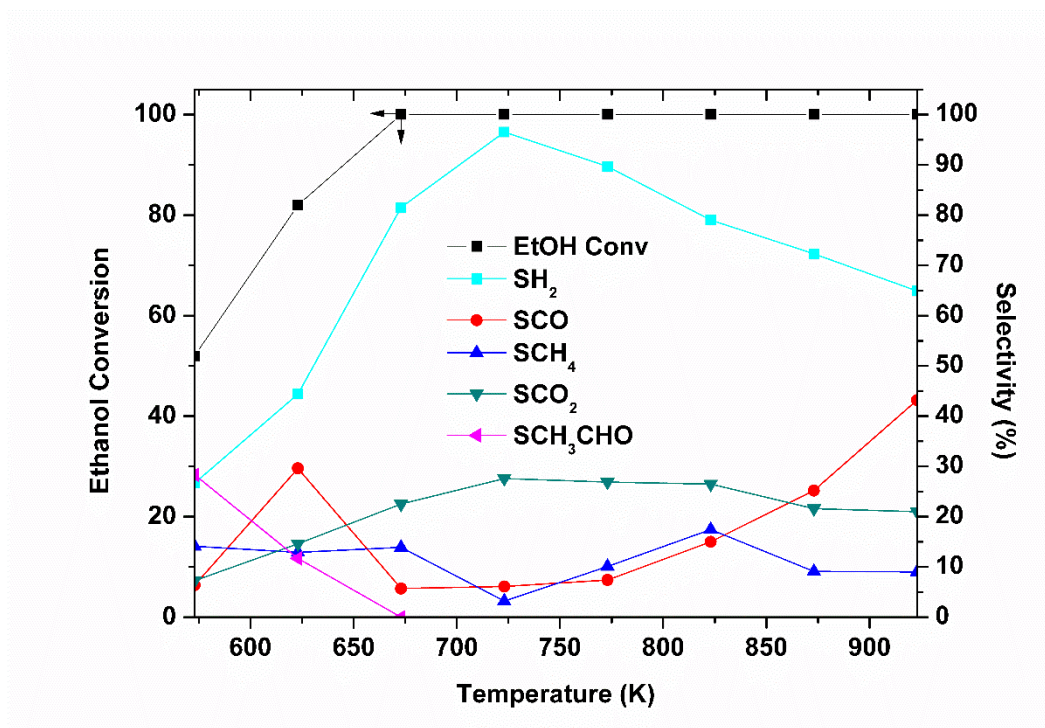


Figure 4.3 Catalyst activity of Co for ESR (molar ratio of H₂O:C₂H₅OH = 3:1, WHSV= 5.244h⁻¹).

It was also interesting that at temperature higher than 723K water formation started. At temperature 773K and 823K CH₄ selectivity was higher and water formation was also higher, which suggest the hydrogenolysis of ethanol can be a dominant reaction in this temperature. The acetaldehyde selectivity was only found at temperatures lower than 673K.

A critical literature survey with this study suggested that by using support, the optimum temperature in terms of hydrogen selectivity is in agreement with Passos et al.[256] Garbarino et al. [222] have also performed the ESR with Co nano-particles and found maximum hydrogen selectivity at 773K but they performed the experiment at interval of 100K and they had not conducted experiments at 723K, which can be an optimum temperature. Moreover, by using few supports with Co, the optimum temperature for hydrogen selectivity is increased but carbon formation gets decreased [105, 123, 254]. The selectivity of constituent gas also varies by using different kind of

supports, because of divergence in reaction pathway selection [266]. The time on stream (TOS) data for 21h with selectivity of different gaseous products during ESR was shown in Figure 4.4. Initially up to 8h, the mixture of generated gas contains H₂, CH₄, CO₂ and CO and afterwards C₄H₁₀ was also found to be present in outlet gas mixture with very less selectivity. Upto 17h, the generated gaseous products did not vary significantly, but after it, the selectivity of H₂ and CO₂ both lowered down and the selectivity of CO and CH₄ were increased abruptly. This behavior suggests the generation of CH₄ at the cost of CO₂ and H₂. The amount of carbon formed on 0.5 g Co-catalyst was found to be 7.26g after 21 h TOS reaction.

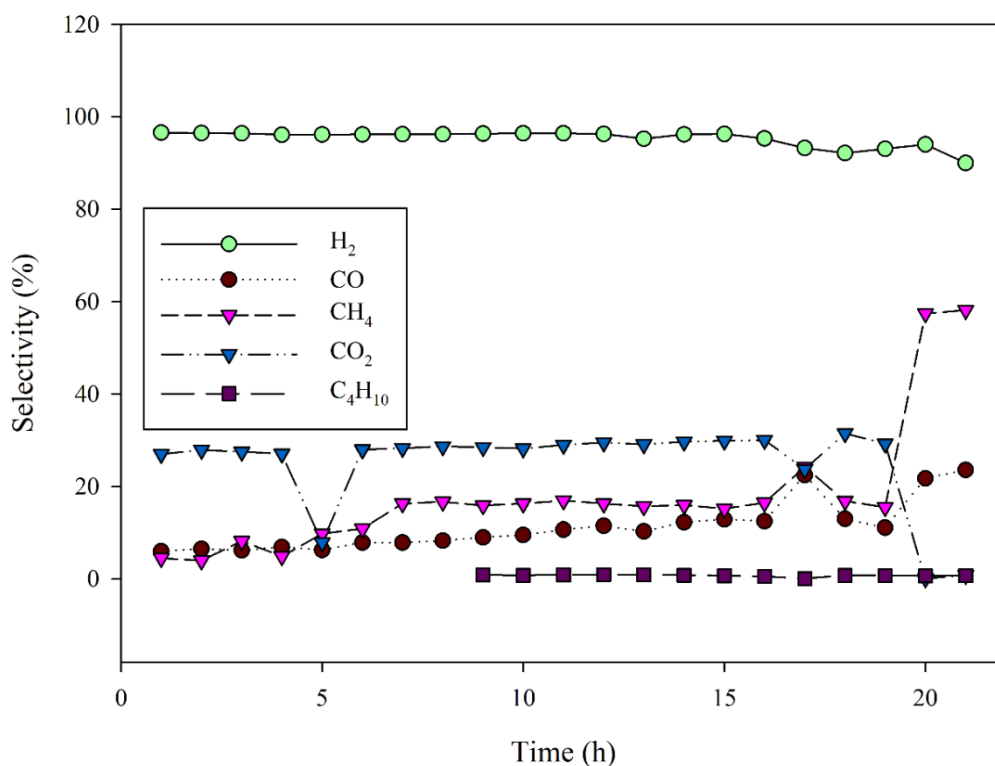


Figure 4.4 Selectivity of gaseous products of ESR on Co catalyst at 723K plotted against TOS (Temperature= 723K, Time= 21h, molar ratio of H₂O:C₂H₅OH= 3:1, WHSV= 5.244h⁻¹).

After performing ESR, catalyst with carbon was characterized with SEM-EDS, HR-XRD and HR-TEM, which are shown in Figure 4.5, Figure 4.6 and Figure 4.7 respectively. The SEM and HR-TEM images confirm formation of a number of carbon filament during ESR. On the basis of the gaseous products formed during reaction, the most probable reactions to generate carbon can be considered either decomposition of CH_4 and CO (eq1.13 and eq1.14) or reaction of hydrogen with CO and CO_2 (eq1.15 and eq1.16). However, the decomposition of CH_4 occurred at higher temperature ($>1173\text{K}$) [91]. Boudard reaction is sensitive upon step edge of catalytic surfaces [98]. Beside these two aforementioned reactions, the hydrogenation reactions may be most favorable reactions for carbon deposition.

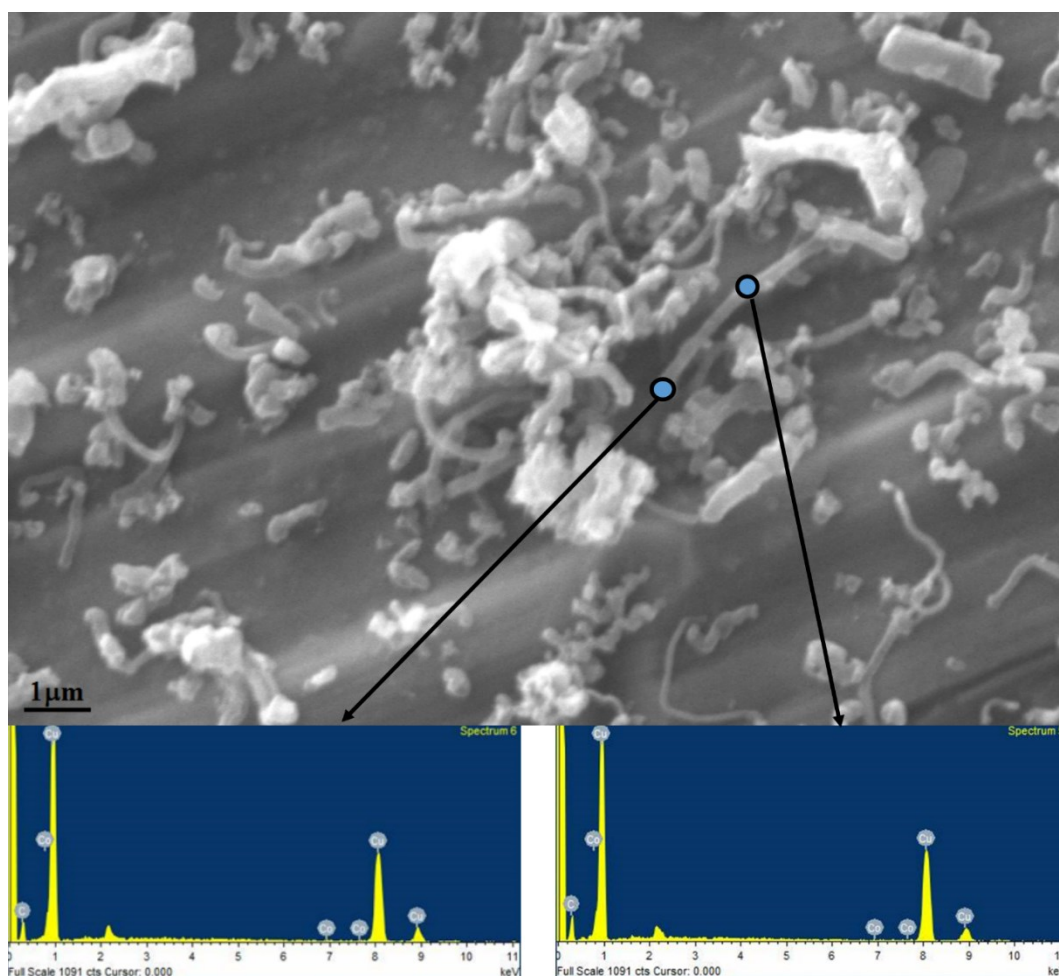


Figure 4.5 SEM-EDS of spent Co-catalyst.

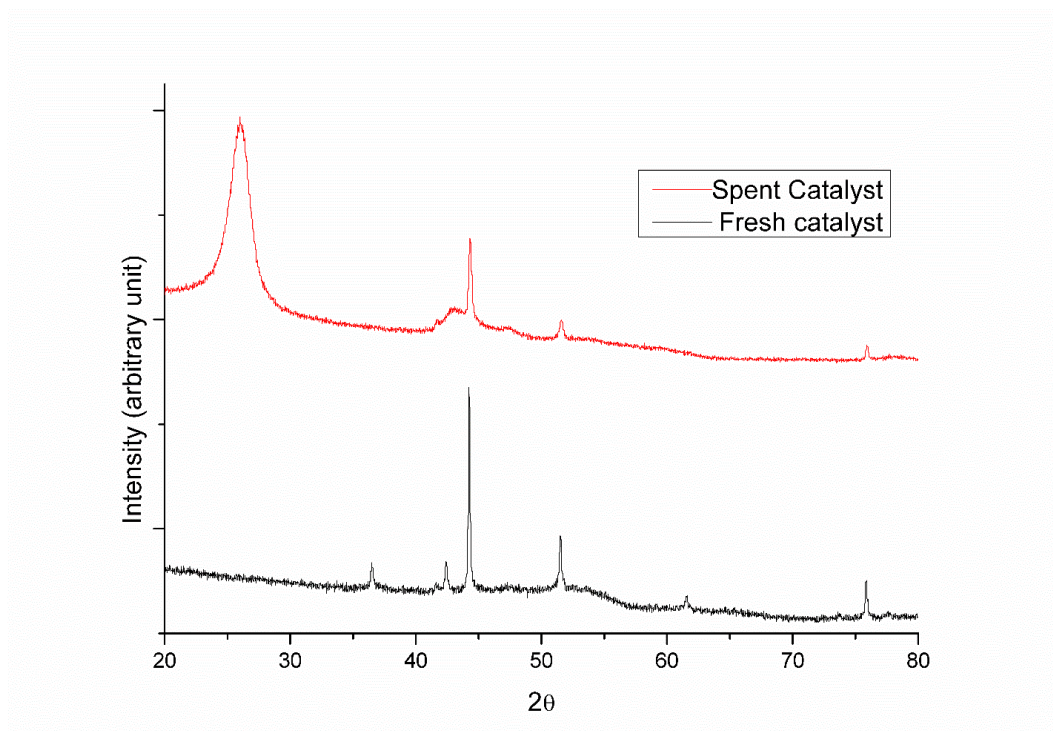


Figure 4.6 HR-XRD of fresh and spent catalyst.

The growth of carbon filament after reaction and presence of cobalt at the tip of filament support the tip growth phenomenon during ESR. However, during EDS analysis the cobalt metal was not only found at the tip of filament as well as in between the filament also. The TEM image analysis also showed filamentous carbon with number of branches initiating from a common point. The carbon nanofilament diameter calculated from image J software was found in 70-80 nm range.

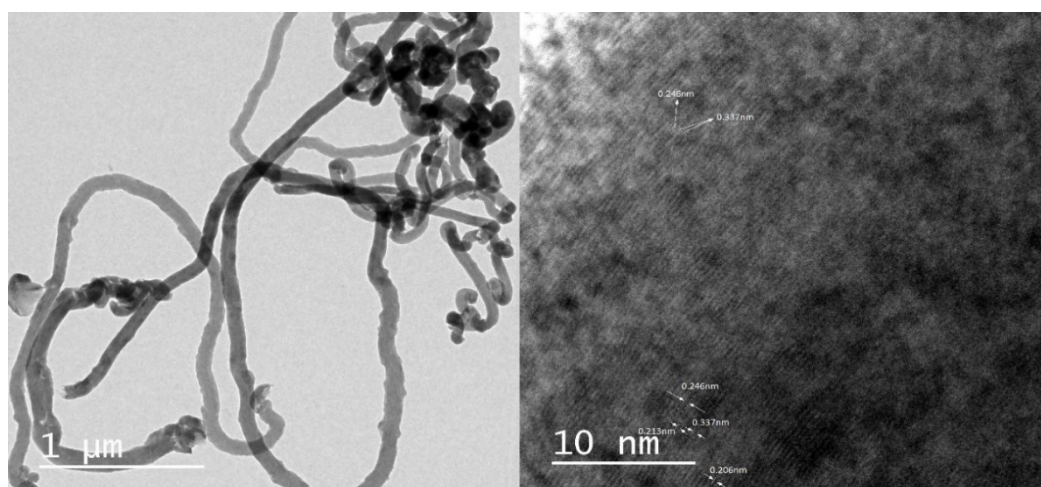


Figure 4.7 TEM and HR-TEM images of Co and carbon nano filament.

However, from SEM image, few carbon filaments with larger diameter can be observed due to agglomeration. It is also interesting to note that after reaction, the size of Co gets reduced and more homogenized with carbon formed during ESR. The HR-XRD of spent catalyst does not display any single peak of CoO phase, whereas, all of the three planes of Co⁰ existed predominantly. Absence of CoO phase indicates the reduction of CoO into Co during the reaction or small concentration of it gets involved in carbon filament formation. Further, HR-TEM image analysis of carbon nanofilament indicates the contribution of (111) and (200) planes in carbon deposition. Both of these planes get sandwiched between the hexagonal primitive form of carbon, which can be seen in Figure 4.7(b).

Conclusion

The time on stream study at 723K in Co⁰ state with (111) plane found that the catalyst remained stable for 19h in terms of H₂ selectivity. The activity of the catalyst starts decreasing after 19h and the main reason for activity loss was due to carbonaceous deposition. The presence of Co metal at the tip of carbon nano filament is confirmed by SEM-EDS analysis of used catalyst. It supported the tip growth phenomenon of carbon filament formation. However, Co metal is also found in between the filaments. It suggests that it may follow Y- junction carbon growth or both ended carbon growth.