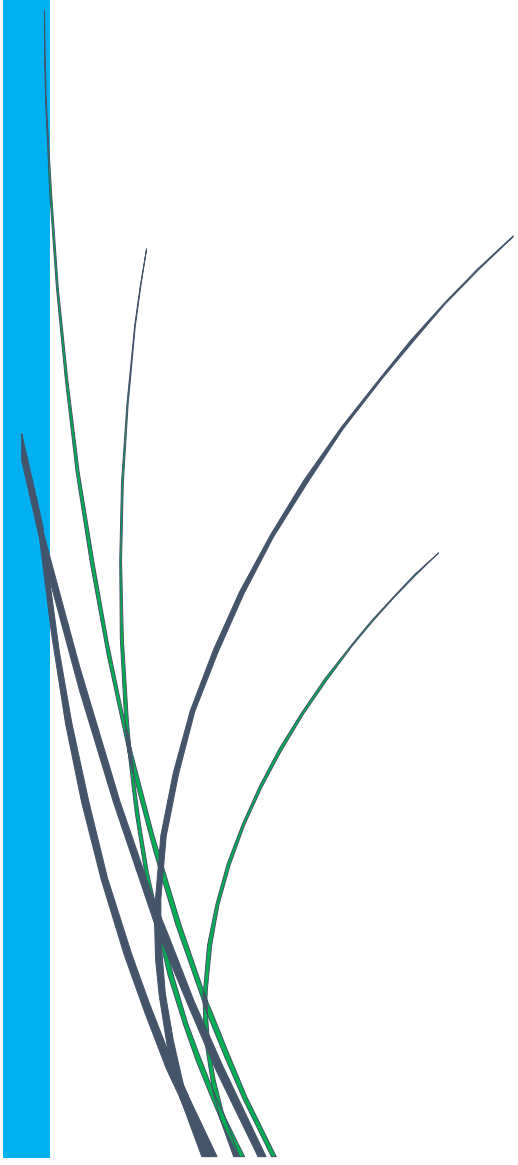
Chapter:8 Promising nano bimetallic oxides of Ni-Co/CeO_2 catalyst for ESR



8.1 Introduction

The solvothermal method involves the simultaneous effect of pressure and temperature with solvent. This exclusive synthesis method leads controlled morphology of nano particles for applications in various fields [122, 348, 349]. Nevertheless, these studies are still constrained up to the precipitation followed by solvothermal treatment, or the reaction among different species within hydrothermal or solvothermal treatment [342, 350-353]. Recently, Hammond et al.[354] synthesized the nano CeO_2 using Deep Eutectic Solvents reline and ethaline (1:2 ChCl: ethylene glycol) mixture by solvothermal treatment. But after solvothermal reaction, they found cloud like suspension, which get precipitated by treatment with water. The precipitation potential of a solvent for metal oxide through solvation of their precursor and solvothermal treatment is still not reported in the literature. The temperature and pH of the reaction medium have major role in precipitation reaction. In solvothermal treatment, pH cannot be controlled, but temperature can be varied. Since the properties of solution differ with pressure and temperature, it may result in different characteristics. The nano-size catalysts are very active for steam reforming of ethanol. The CeO_2 based support is highly active in steam reforming reactions because it has good oxygen mobility even during the reaction [355]. As reported in chapter 3, the synergistic effect of Ni and Co was found positive for ESR. Therefore, CeO_2 supported bimetallic Ni-Co catalysts were selected for further studies.

8.2 Experimental

8.2.1Catalyst preparation

Four types of catalysts were prepared by solvothermal precipitation. The nomenclature of the catalysts is as follows: CeO_2-SP, 20% Co/CeO_2 (Co/CeO_2-SP), 20% Ni/CeO_2 (Ni/CeO_2-SP) and 20%Ni-Co/CeO_2 (Ni-Co/CeO_2-SP). For the preparation of CeO_2, 0.25M solution (5.42 g Ce $(NO_3)_2.6H_2O$ solubilized in 50 ml of ethanol) was taken

in Teflon vessel of 200 ml, which was kept in autoclave reactor for different durations (2h, 4h and 6h) into the furnace at different temperature (373K, 393K, 413K, and 433K). After cooling at room temperature, the precipitate was separated by centrifugation at 14500 rpm for 5 minutes. The liquid part was decanted and the solid precipitate was dried at room temperature without washing to find out whether the nitrate impurities persist after precipitation or not. The XRD analysis of the precipitate confirmed that pure CeO_2 was formed directly by solvothermal process (reported in section 8.3.1.3). The obtained CeO_2 precipitate (CeO_2-P) was calcined in a furnace at 673K for 3h. The calcination temperature was determined by thermo gravimetric analysis (TGA) of CeO_2-P.

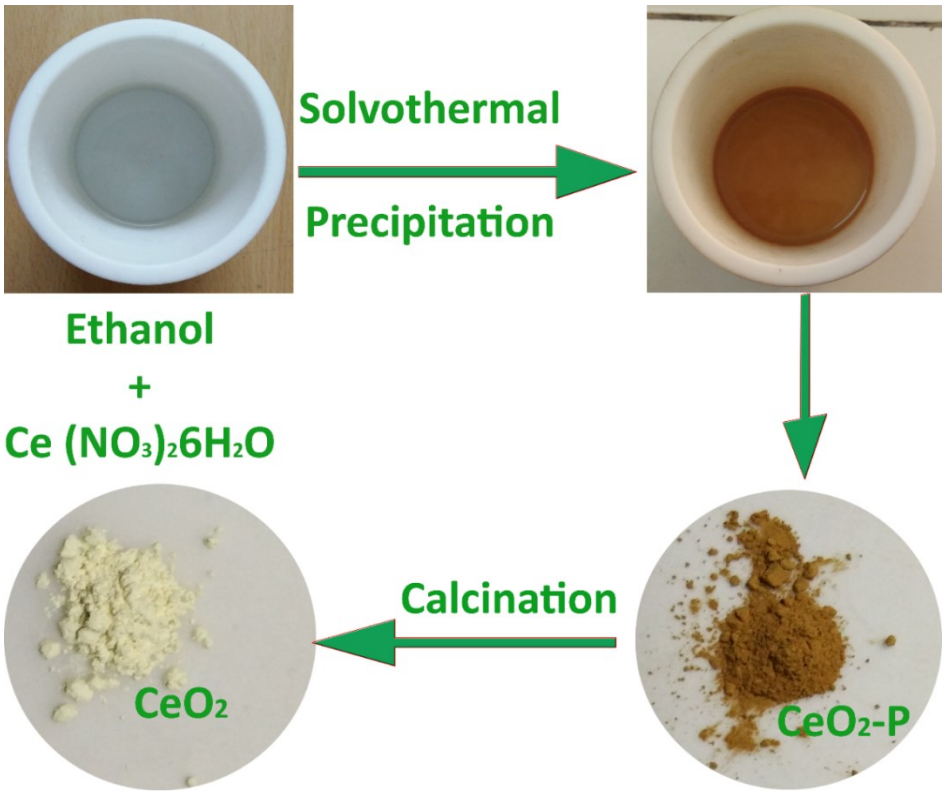


Figure 8.1 The colour difference at difference stage of reactions.

The photographs of the precipitate before calcination and after calcination are shown in Figure 8.1. The color of dried precipitate before calcination was brown which turned yellowish-white after calcination. The color of the dried precipitate indicates that

some organic species may be present in the sample which was completely removed after calcination.

Similarly, 20%Co/CeO_2 and 20%Ni/CeO_2 were prepared by adding the stoichiometric amount of Ni $(NO_3)_2.6H_2O$ and Co $(NO_3)_2.6H_2O$ in the 0.25 M solution of Ce precursor individually. 20%Ni Co/CeO_2-SP was prepared by mixing the stoichiometric concentration of Ni $(NO_3)_26H_2O$, Co $(NO_3)_26H_2O$ and Ce $(NO_3)_26H_2O$ in 50ml ethanol. The mixture was taken in Teflon vessel of 200 ml, which was kept in autoclave reactor at optimized temperature and duration (obtained after CeO_2 precipitation). The obtained precipitate of catalysts were calcined at 823K for 3h because the maximum temperature of ESR performance for this study was opt 823K.

The three bimetallic catalysts having different compositions of 10, 15 and 20% Ni-Co/CeO_2 were prepared by co-precipitation cum solvothermal precipitation method. The percentage of Ni-Co was equivalent to $NiCo_2O_4$. First of all, the $NiCo_2O_4$ was prepared by co-precipitation method was described elsewhere [356]. In brief, the aqueous solution of both precursors (Ni $(NO_3)_2.6H_2O$ and Co $(NO_3)_2.6H_2O$) were prepared in 1:2 (Ni: Co) molar ratio and precipitated with the help of 150 ml KOH (1M) solution under vigorous stirring and N_2 bubbling condition. The precipitated blue colour mixture was continuously stirred for 6h and then separated by centrifugation at 5000 rpm. The hot distilled water was used for washing three times and then dried in oven overnight. The calcination of mixture was done at 623K for 21h. Next, a part of the prepared $NiCo_2O_4$ was added in required amount into the ethanol solution of Ce $(NO_3)_2.6H_2O$. The ultrasonication of the slurry was performed for dispersion for 15 minutes. Then, the slurry was kept in Teflon vessel of 200 ml, in autoclave reactor for 4h into the furnace at 413K. After cooling at room temperature, the slurry was centrifuged at 14500 rpm for 5 min. The obtained solid was calcined at 773K for 2h.

8.2.2 ESR performance Test

ESR reaction was performed in vertical quartz reactor having internal diameter 9 mm. 100 mg of catalyst was kept on quartz wool bed prepared at center of the reactor. The effect of different stoichiometric ratio of water and ethanol (3:1, 6:1 and 12:1) was also studied. The feed rate of ethanol water mixture was kept constant 4ml/h. The time on stream experiment was performed over the optimized reaction conditions.

8.3 Results and discussion

8.3.1 Characterization of catalyst

8.3.1.1 Textural characterization

The textural properties surface area and pore volume of the catalysts are listed in table 8.1. It is apparent from the table that the specific surface area and pore volume both reduced with increasing Ni-Co concentration. It may be due to blocking of some pores of CeO_2 by Ni-Co. Meanwhile, the surface area and pore volume data of Co/CeO_2-SP, Ni/CeO_2-SP and Ni-Co/CeO_2-SP catalysts show that the catalysts prepared by solely solvothermal method have higher specific surface area and pore volume compared to the precipitation cum solvothermal method.

Table 8.1 Surface area and pore volume of CeO_2 as well as CeO_2 supported catalysts

Catalyst	Surface Area (m^2/g)	Pore Volume (ml/g)
CeO_2	95.2	0.048
Ni/CeO_2-SP	78.3	0.047
Co/CeO_2-SP	64.1	0.038
$NiCo_2O_4$	47.5	0.025
10 Ni-Co/CeO_2	63.2	0.037
15 Ni-Co/CeO_2	50.4	0.028
20 Ni-Co/CeO_2	35.9	0.026
20 Ni-Co/CeO_2-SP	45.1	0.029

8.3.1.2 Thermal analysis of precipitate

The TGA-DSC analysis of CeO_2-P shown in Figure 8.2 revealed that the whole process of decomposition was completed in two steps. The initial weight loss 2% upto

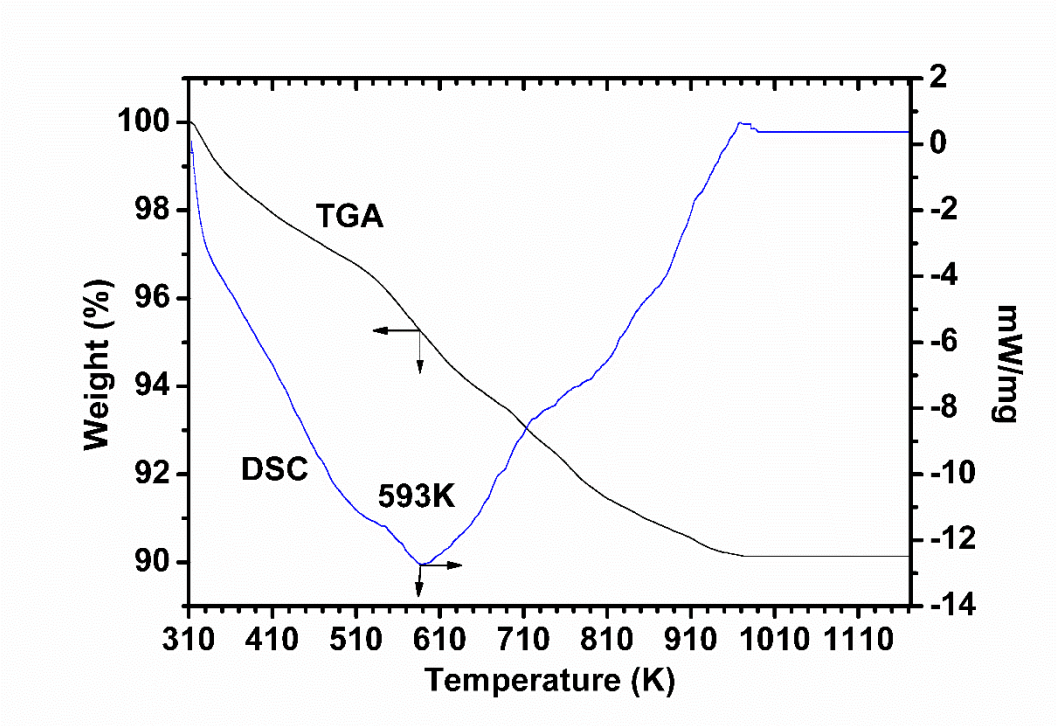


Figure 8.2 TGA-DSC analysis graph of CeO_2 –P with temperature.

393K in the first step may be due to surface adsorbed moisture. In the second step, the major weight losses of 8% occurred within 498-950K. The decomposable species present in the sample get lost below 950K. The DSC curve confirmed the endothermic process during complete weight loss. The weight loss may be due to decomposition of ethoxide, carbonate and crotonaldehyde species present in the sample, confirmed from ATR-FTIR analysis.

8.3.1.3 XRD analysis

The XRD pattern of the precipitate formed by solvothermal process ($Ce(NO_3)_2.6H_2O + C_2H_5OH$) is depicted in Figure 8.3. The 2θ values of the precipitate were 28.54° (111), 33.07° (200), 47.47° (220), 56.33° (311), 59.07° (222), 69.40° (400), 76.68° (331) and 79.06° (420) which confirmed that the face centered cubic crystallite of CeO_2 was formed directly by solvothermal process (JCPDS 81-0792). The diffractogram does not show any other peak, and it indicates that the CeO_2 was synthesized in pure form.

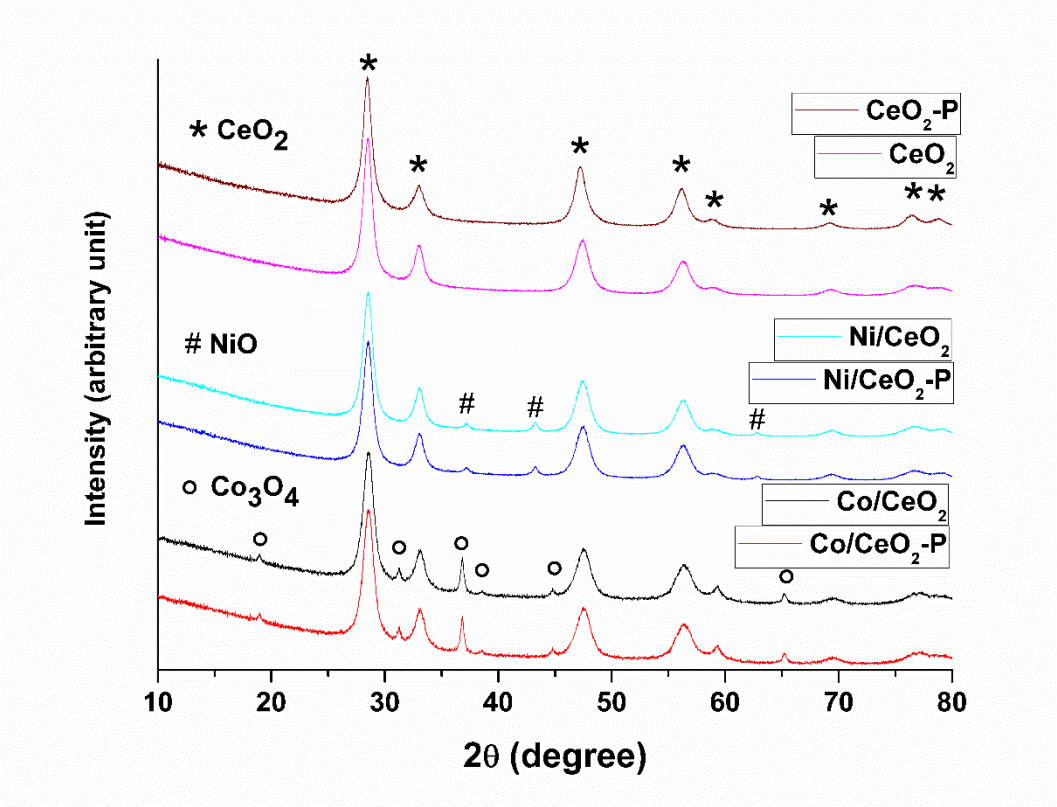


Figure 8.3 HR-XRD of CeO_2, 20Ni/CeO_2-SP, 20Co/CeO_2-SP from top to bottom.

For Ni/CeO_2-SP and Co/CeO_2-SP samples XRD pattern revealed that along with CeO_2, NiO and Co_3O_4 were also formed respectively.

The XRD pattern of $NiCo_2O_4$, 10Ni-Co/CeO_2, 15Ni-Co/CeO_2, 20Ni-Co/CeO_2, and 20Ni-Co/CeO_2-SP are presented in Figure 8.4. The 2θ values 19.06° (111), 31.38° (220), 36.97° (311), 38.68° (222), 44.97° (400), 59.58° (511), 65.49° (440) correspond with cubic and face-centered crystallite of Co_3O_4 JCPDS (65-3103). The XRD pattern of Ni/CeO_2 has shown the face centred cubic phase of NiO at 2θ value 37.39°, 43.24° and 62.70° were matched with JCPDS (47-1049). The $NiCo_2O_4$ spinel prepared by co-precipitation method consisted of face centred cubic crystallite at 2θ values 18.92° (111), 31.15° (220), 36.70° (311), 38.40° (222), 44.63° (400), 55.43° (422), 59.13° (511) and 64.97° (440) are in according to JCPDS (73-1702).

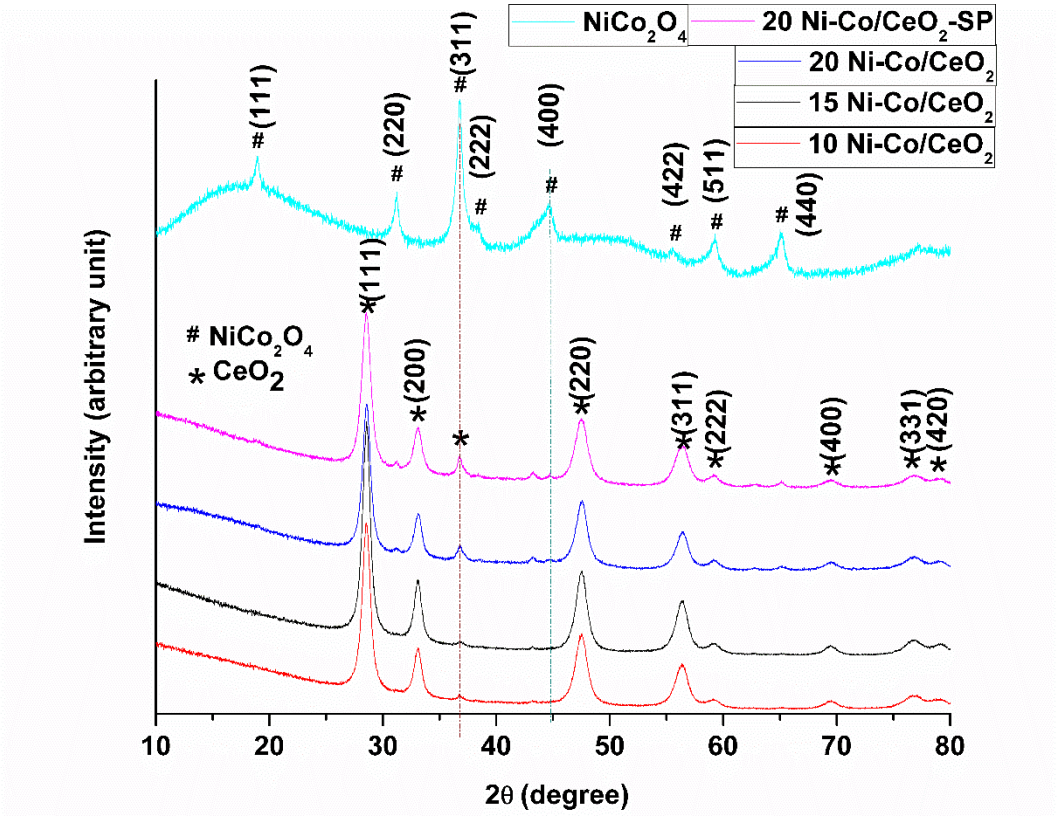


Figure 8.4 HR-XRD of $NiCo_2O_4$, 20Ni-Co/CeO_2-SP, 20Ni-Co/CeO_2, 15Ni-Co /CeO_2, and 10Ni-Co/CeO_2 from top to bottom.

When ethanolic solution of $Ce(NO_3)_2.6H_2O$ was added into solid $NiCo_2O_4$ (spinel) and treated solvothermally, the spinel structure of $NiCo_2O_4$ disappeared. Similarly, it can be visualized from the diffractograms that no formation of $NiCo_2O_4$ spinel structure took place in all the samples containing CeO_2. In case of Ni-Co/ CeO_2 catalyst, concentration of CeO_2 was 80%, therefore the peak of Co_3O_4 and $NiCo_2O_4$ overlapped with CeO_2 at 2θ values 36.97° and 59.58°.

8.3.1.4 FTIR analysis

Yee et al. studied effect of ethanol on the surface of CeO_2 based catalysts by *in situ* FTIR spectroscopy [357, 358]. They reported that with increasing temperature carbonate species dominantly persist on CeO_2 surface, while ethoxy and acetaldehyde species decomposed. The FTIR spectra of each precipitate obtained in this study was almost corresponding to the spectra obtained at 623K by Yee et al. [89] for CeO_2 based

catalysts. It indicates that the adsorbed carbonate species with two vibrational symmetric modes (1419 and 1335) and one asymmetric mode (OCO) (1536) were dominantly found on surface of precipitated CeO_2. These are the surface adsorbed species, because the carbonate of Ce or other active metal was not confirmed in XRD spectra. Beside, those peaks, the small intense peaks of C-O species for ethoxide (1020 and 1048) and crotonaldehyde (1649) were also found. After calcination, all these peaks disappeared but small broad peaks remained at 1330 cm^{-1} which can be assigned for Ce-O-Ce [359].

The FTIR of Co/CeO_2 and Ni/CeO_2 catalyst precursor obtained after solvothermal precipitation reaction have also common peaks with CeO_2 at wavenumber 1640 cm^{-1} and 1419 cm^{-1}. However, peak at 1536 cm^{-1} of CeO_2 was shifted at 1556 cm^{-1} for Co/CeO_2 and Ni/CeO_2. This shifting might be due to influence of co-ordination between Ce and O with Ni or Co. After calcination, these peaks were disappeared and peak at 1330 cm^{-1} was become prominent.

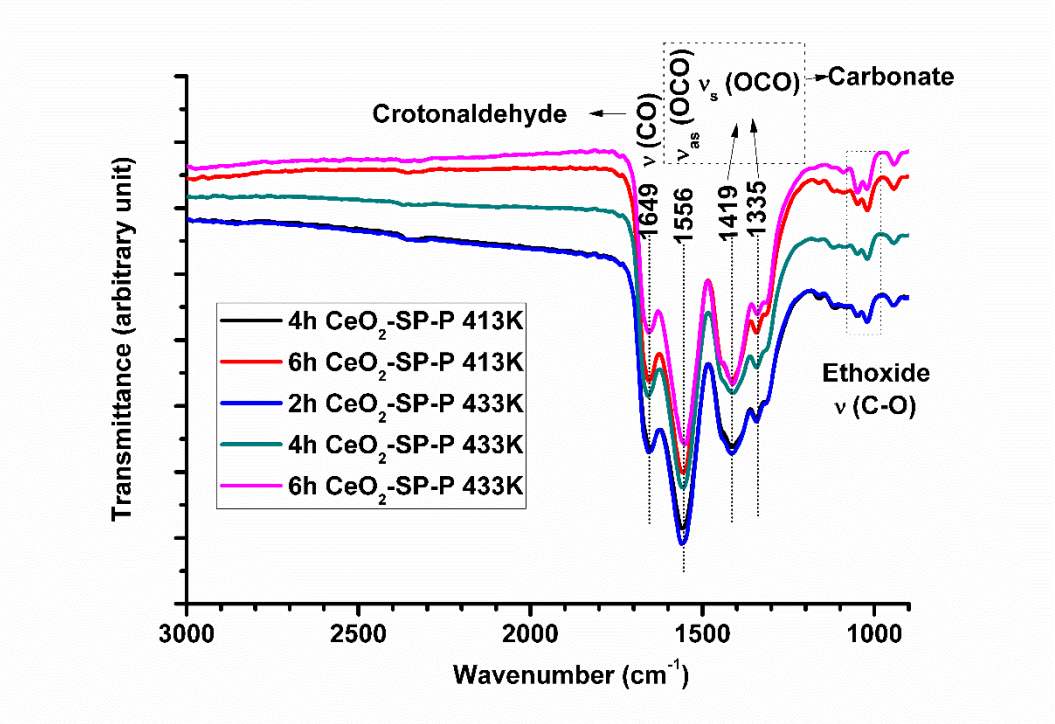


Figure 8.5 ATR-FTIR of the CeO_2-SP-P after treatment with different temperature and time duration.

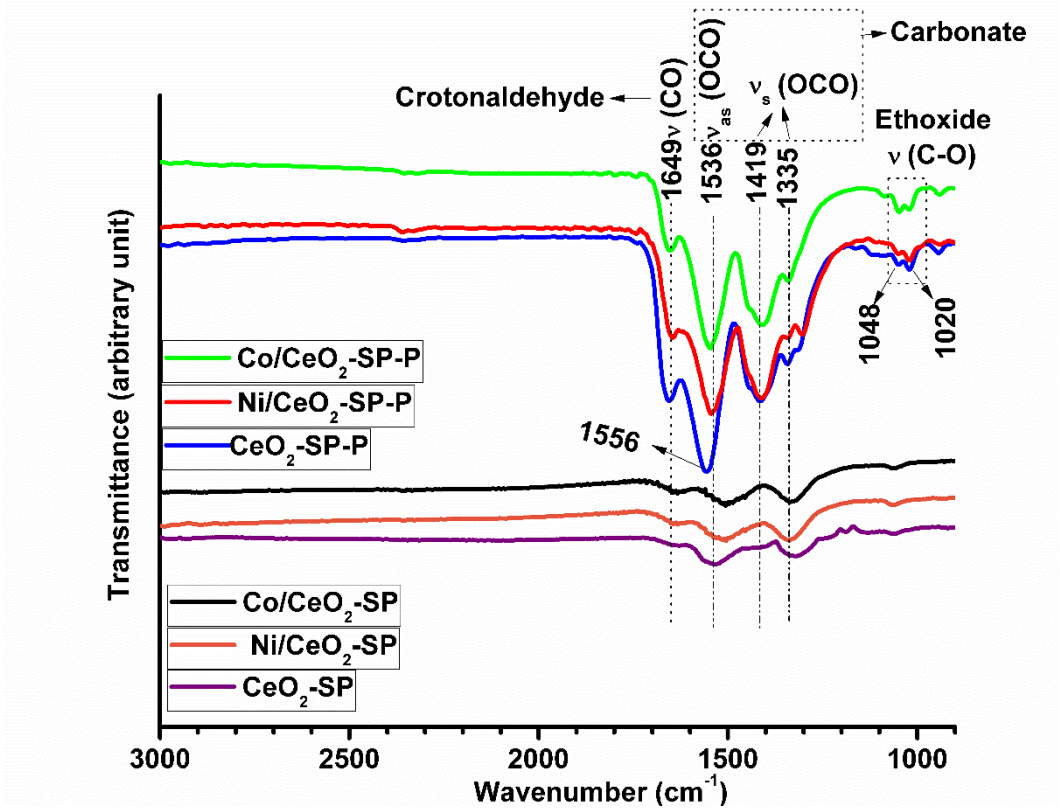


Figure 8.6 ATR-FTIR of precipitate and their respective metal oxides.

The fingerprint region contains sharp peak at 525 cm^{-1} for Ce-O bond. Hence, CeO_2 formation was confirmed by an agreement of HR-XRD and FTIR data of prepared catalyst. The sharp peak at 659 cm^{-1} and 559 cm^{-1} can be assigned for Co_3O_4, whereas in case of $NiCo_2O_4$ 655 cm^{-1} and 553 cm^{-1}, the peak at 655 cm^{-1} get shifted to 662 cm^{-1} for each Ni-Co/CeO_2 catalyst, which may be due to an interaction of Ni and Co with CeO_2. However, it is complicated to interpret the peaks after 600 cm^{-1} for Ni-Co/CeO_2 catalyst, because in that region the shoulder peak of CeO_2 (about 525 cm^{-1}) with NiO and Co_3O_4 got overlapped. It is clear from the figure that the peak intensity got reduced at 659 cm^{-1} as compared to 600-500 cm^{-1} region because of increase in concentration of CeO_2. The peak intensity was higher for 10Ni-Co/CeO_2 at wave number 1330 cm^{-1}, but lowest at 662 cm^{-1}, because the concentration of CeO_2 is higher in 10Ni-Co/CeO_2 and concentration of NiO and Co_3O_4 were higher in 30 Ni-Co/ CeO_2.

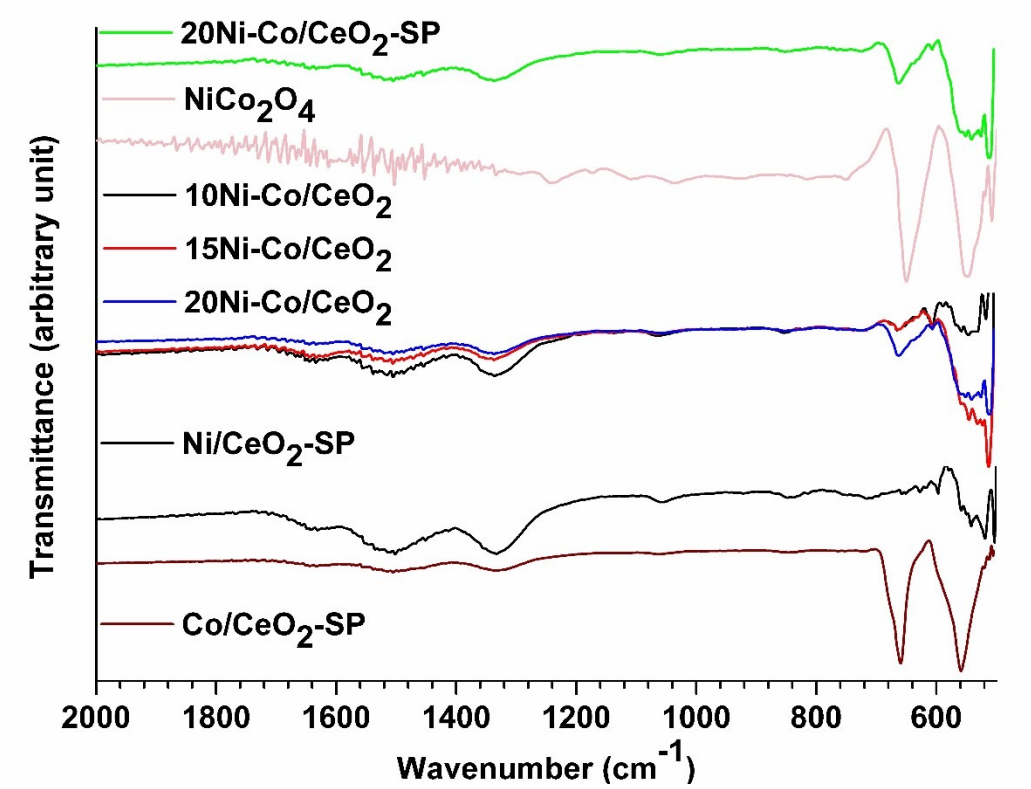


Figure 8.7 Comparative ATR-FTIR of each bimetallic and mono metallic catalyst.

8.3.1.5 Morphology analysis

The Transmission electron microscope (TEM) imaging analysis of CeO_2-SP is shown in Figure 8.8. The high-resolution images of CeO_2-P and CeO_2 show the crystalline nature of particles with dominant (111) planes. From Figure 8.8a and 8.8b, the average particle size calculated using image J software for CeO_2-P and CeO_2 were within 9.7-10 nm range. It is interesting to note that crystal development of CeO_2-P occurred even before calcination. Even after calcination of CeO_2-P at 413K, the nano-size particles remain intact. But calcination of CeO_2-P at 433K produced three different forms (rod, cubic and hexagonal) of the particles with 95nm average particle size (Figure 8.8e and 8.8f). It indicates that nucleation of particles is higher with an increase in temperature during solvothermal treatment.

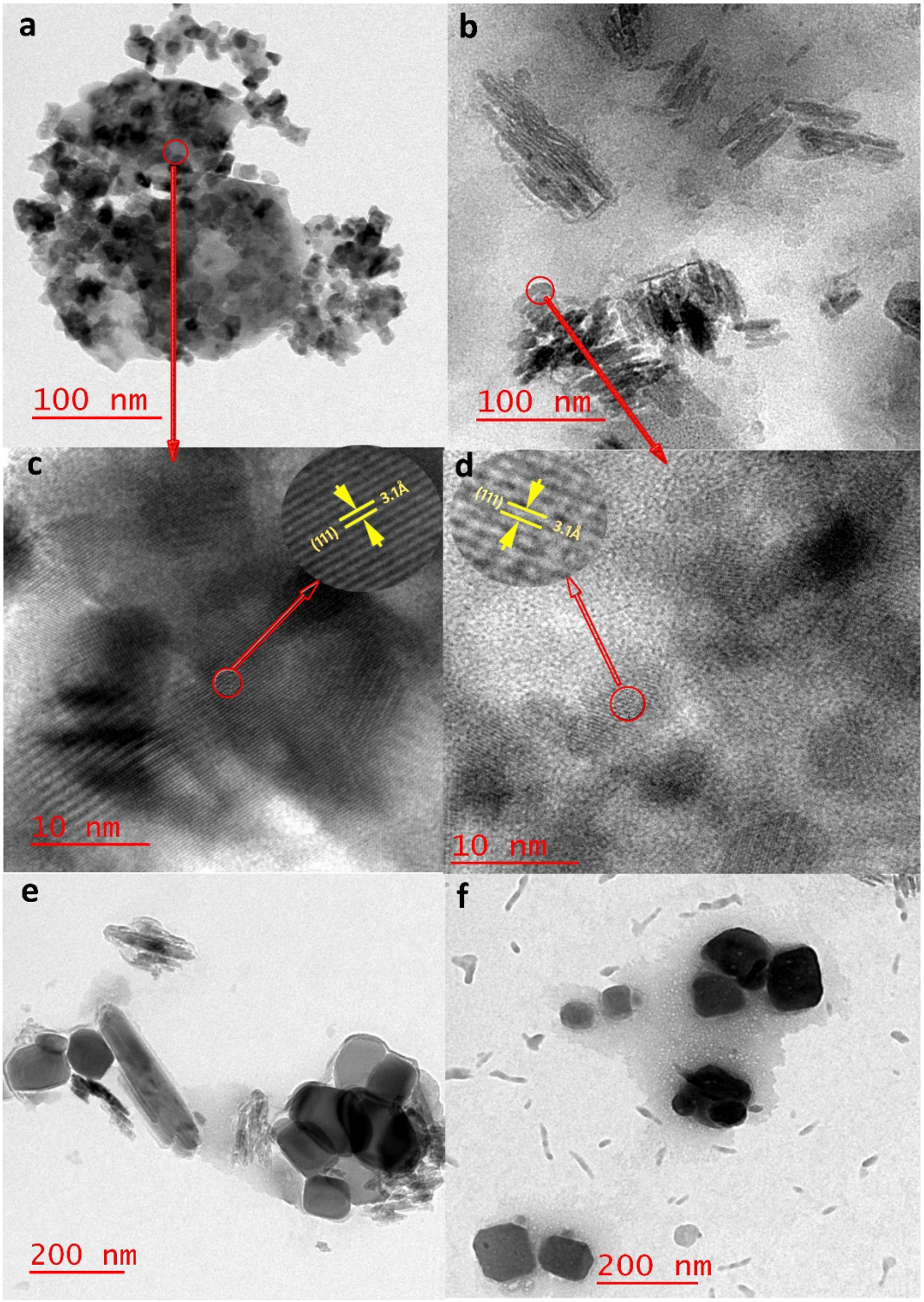


Figure 8.8 TEM image of CeO_2-SP-P(a), CeO_2-SP (Solvothermal treatment at 413K for 4h) (b), CeO_2-SP (Solvothermal treatment at 413K for 6h) (e and f) and HR-TEM image of CeO_2-SP-P (c), CeO_2-SP (d).

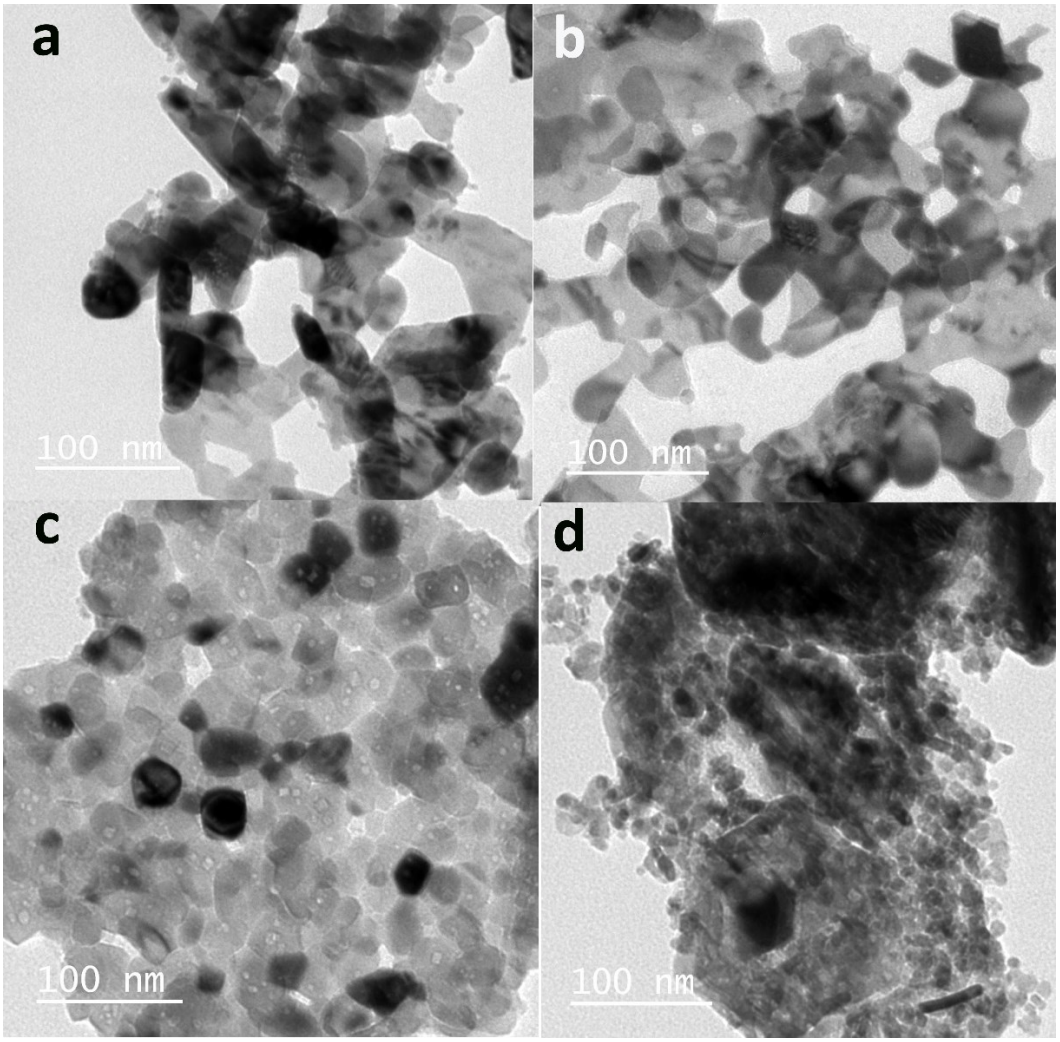


Figure 8.9 TEM image of Ni/CeO_2-SP (a), Co/CeO_2-SP (b), 20Ni-Co/CeO_2-SP (c), and 20Ni-Co/CeO_2 (d).

The TEM images of Co/CeO_2 and Ni/CeO_2 are also presented in Figure 8.9a and 8.9b respectively. The average particle size is 20-25 nm which is higher than CeO_2. It may be due to high-temperature calcination of Co/CeO_2-P and Ni/CeO_2-P as compared to CeO_2.

8.3.2 ESR performance test

ESR performance product distribution graph with ethanol conversion and selectivity of different gases verses temperature are presented in Figure 8.10. The product gas selectivity variation can be easily observed from the graph with respect to Ni-Co concentration. The ethanol conversion also increases with increasing concentration of

active metal catalyst. Independently, Ni shows less ethanol conversion compared to Co at lower temperature, but above 773K, the ethanol conversion was almost complete for each catalyst. In case of bimetallic catalyst with CeO_2, the spinel form of catalyst didn't exist but the synergistic effect of Co and Ni resulted into almost constant ethanol conversion within 673-873K temperature. The double carbon content product selectivity was higher in Co/CeO_2 compared to Ni/CeO_2. The C_2H_4 and CH_3CHO selectivity were reduced for each $Ni\text{-}Co/CeO_2$ catalyst.

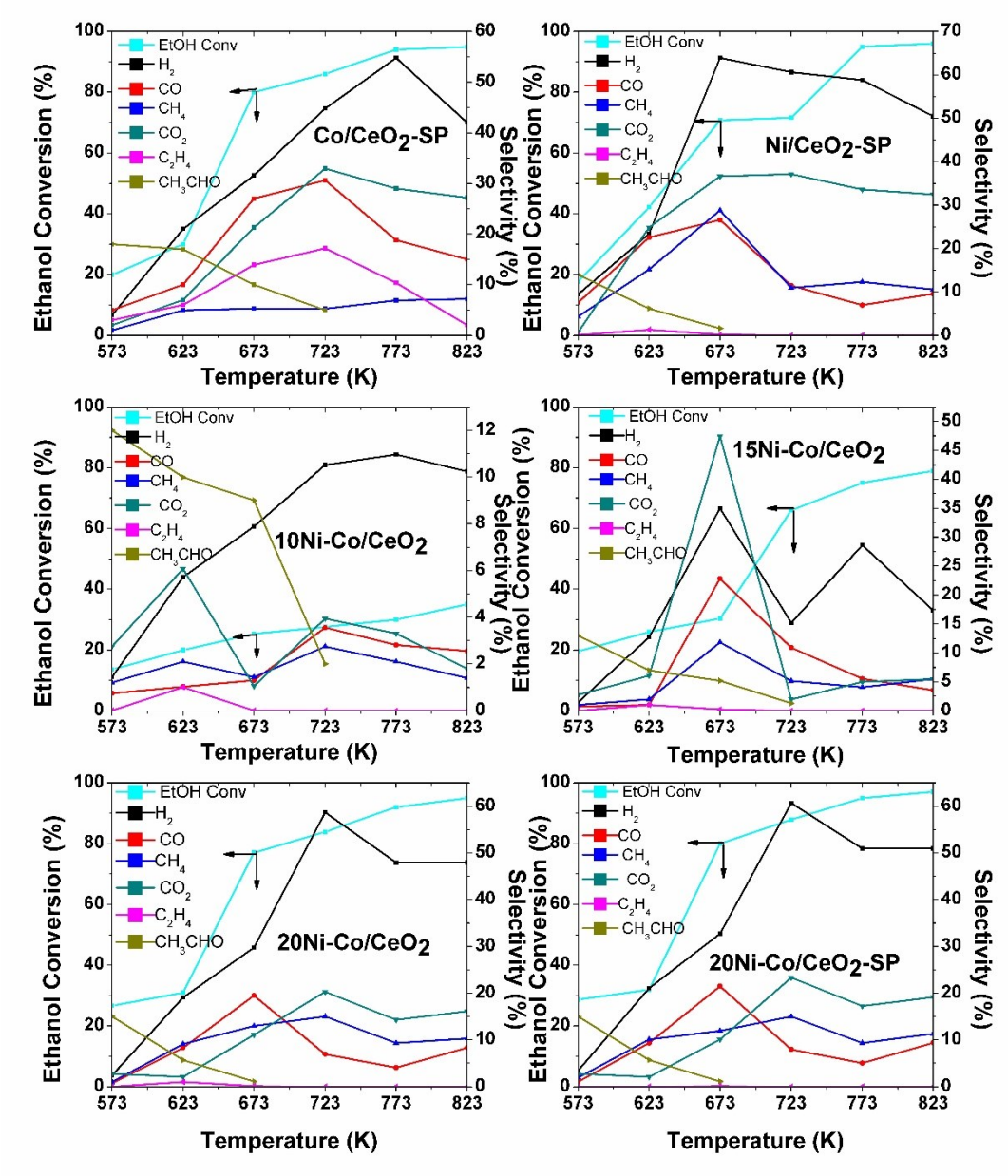


Figure 8.10 ESR performance and product selectivity with temperature.

The CH_3CHO formation was commonly observed for CeO_2 based catalyst, but there is some contradiction regarding acetone or acetylene formation. Two different groups, Song et al. and Wang et al. [343, 360] reported the presence of acetone, whereas Machocki et al. and Loven et al.[67, 68] reported C_2H_4 formation. Loven et al. have suggested the possibility of acid cites favoring the C_2H_4 formation considering the work reported by Nishiguchi et al.[361]. The effect of particle size during ESR by Soyakal et al. [339] revealed that nano CeO_2 facilitates the C_2H_4 formation at each temperature. In present study as well as the work reported by Machocki et al. are based on nano CeO_2 based support, the results are in agreement. Therefore, the acetone formation was completely absent in the liquid product for every catalyst. The product gas selectivity was almost similar to the bare Ni and Co catalysts as found in chapter 3. The notable point is in the presence of 20% active metals supported on CeO_2, the activity is equivalent to the bare active metals.

The optimization of water/ethanol ratio on 20Ni-Co/CeO_2 catalyst for ESR was represented in Figure 8.11. From the figure it is clear that the ethanol conversion, H_2 selectivity and CO_2 selectivity get prominently increased with increase in the concentration of water in feed mixture. However, CO selectivity was also increasing but with less proportion. The selectivity of CH_4 and CH_3CHO were significantly reduced by increasing the water content in feed mixture. It may be due to reformtion of CH_4 with water producing syn-gas and CO_2 as described in chapter 1 by equations 1.22 and 1.23. The C_2H_4 also reacts with H_2O forming CO and CO_2 as described by eqs1.18 and 1.19. Hence, the concentration of CO and CO_2 both get increased by increasing the water concentration. The time on stream study suggested that the product gas distribution was stable up to 10 h duration.

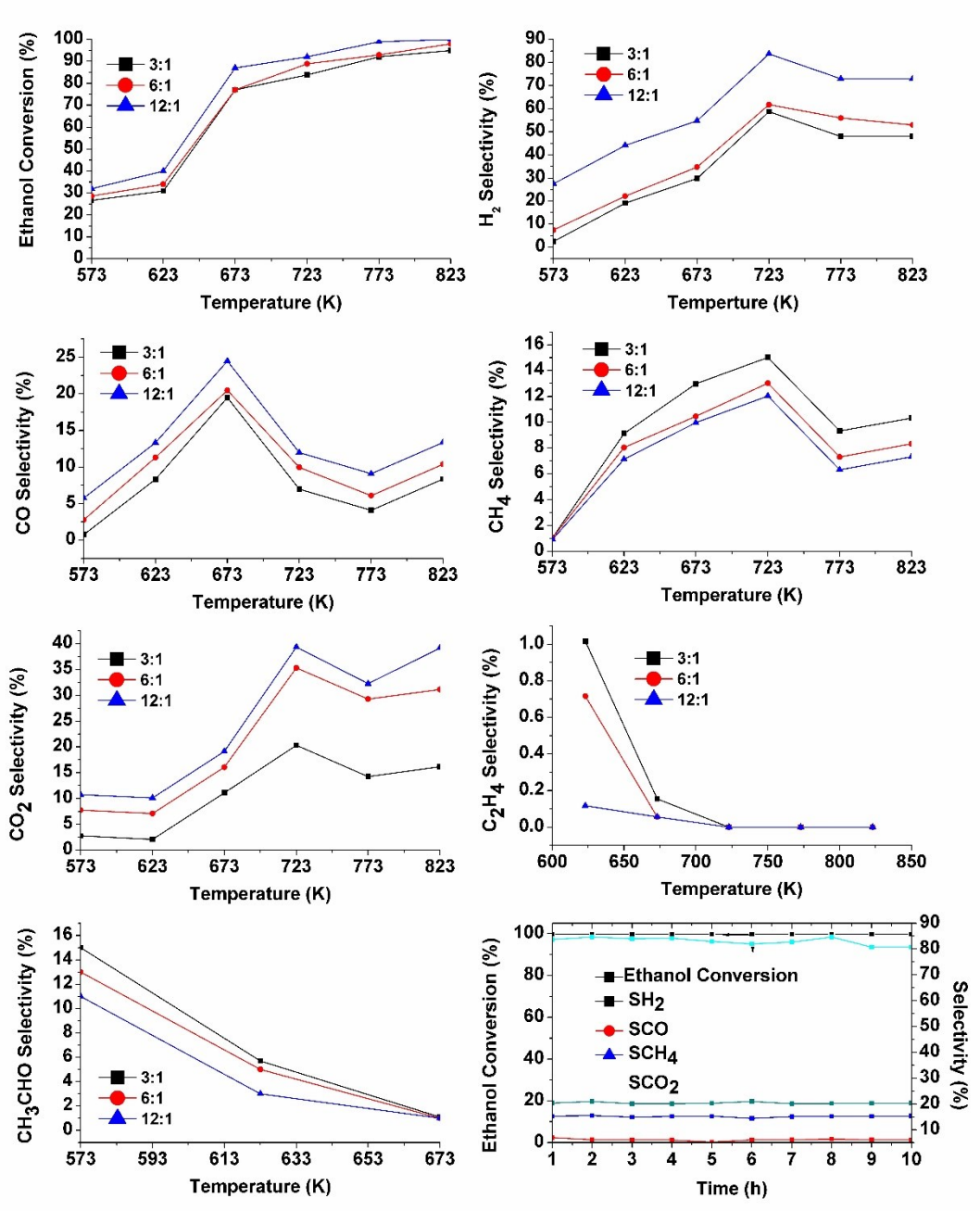


Figure 8.11 Selectivity of different product gases with variation in ethanol water molar ratio for 20Ni-Co/CeO_2 with temperature. Time on Stream study performed at 773K, Ethanol: water (12:1), WHSV= 35.4h^{-1}.

8.4 Conclusion

A substantial route of nano sized metal oxide is developed by using ethanol solvent and solvothermal treatment. This method was termed by us as a solvothermal precipitation and the catalyst prepared by this method was found highly active for ESR.