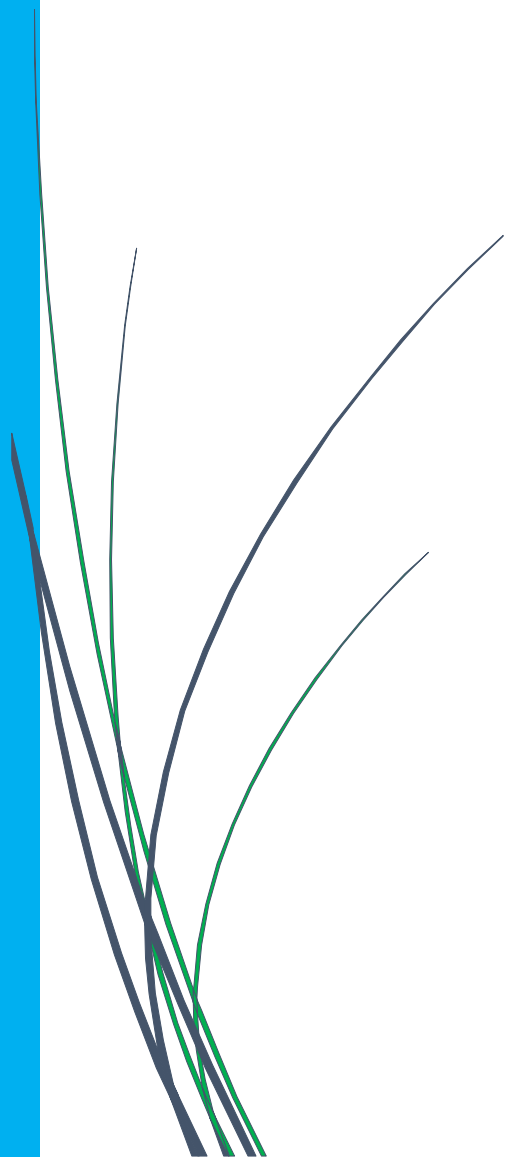# Chapter:3

Blank tests and active non-noble catalysts

3.1 Introduction

Prior to performing the experiments with synthesized catalysts, it is necessary to perform the experiments under same operating conditions in absence of catalyst to observe whether reactor wall or quartz wool had any reactivity. The quartz wool was used to support the catalyst bed in the reactor.

There are a number of non-noble catalysts used for the ESR, among those Ni and Co metals are reported to be highly active catalysts in the literature. The Ni and Co can form spinel structure and may affect the desired gas selectivity during ESR [119, 158, 240]. However, the catalytic activity of Ni spinel structure with Mn, Fe, Al and Zn as well as active Ni supported on different spinel are reported [21, 27, 77, 125, 241-247]. Most of the works were studied on $MgAl_2O_4$ and $ZnAl_2O_4$ as a support and Ni and Rh as active metals. The substitution of B sites of spinel with other metals or coexistence of two metals in the stoichiometric ratio at B sites were also studied by Aupretre et al. [241]. The addition of Pr in $MgAl_2O_4$ was reported by Barroso et al. [242] for the product gas stability with time on stream. Szijjarto et al. have reported the effect of promoter with Ni-Co/$MgAl_2O_4$ and achieved 100% ethanol conversion at 773K with significant hydrogen selectivity [245]. Galetti et al. [125, 246] were initially reported 48.2% ethanol conversion for Ni/$ZnAl_2O_4$-CeO_2 and later on by varying the precursor used in catalyst synthesis and pre-treatment condition they achieved 88% ethanol conversion at 923K. Anjaneyulu et al. [241] have found 100% ethanol conversion with Ni/$ZnAl_2O_4$ at 773K. Both of these studies had different molar ratio of ethanol-water fed mixture and the amount of catalysts.

The catalytic activity of $NiCo_2O_4$ is still unrevealed for ESR reaction. The comparative study of Co, Ni and $NiCo_2O_4$ might give an insight in the reaction pathway governed by these active metals. Therefore, in this study, the ESR performance was

studied with Ni, Co and $NiCo_2O_4$ from 573K-823K to find out the possible reaction pathways involved during ESR with these catalysts.

3.2 Experimental

3.2.1 Preparation of catalyst

Three kinds of catalyst Ni, Co and $NiCo_2O_4$ were prepared to perform the ESR. The $NiCo_2O_4$ was prepared by co-precipitation method from AR grade nitrate precursor of Ni $(NO_3)_2.6H_2O$ and Co $(NO_3)_2.6H_2O$ supplied by MERCK with 97% purity. The aqueous solutions of both precursors were prepared in 1:2 (0.01 mol Ni precursor and 0.02 mol Co precursor were dissolved in 50 ml of double distilled water) molar ratio. The solution was taken into beaker and 1M aqueous solution of KOH (supplied by MERCK with 85% purity) was added drop wise under vigorous stirring conditions and N_2 bubbling condition until solution achieved pH 10. The agitation of mixture was continued for 6h and then precipitate was separated by centrifuge at 5000 rpm. Mixture was washed three times with hot deionized water. The obtained precipitate was dried in oven overnight and then calcined at 823K. The Ni and Co catalyst were prepared by in-situ calcination in argon atmosphere, from their oxalate precursor (AR grade $CoC_2O_4.2H_2O$ and $NiC_2O_4.2H_2O$) at temperature 823K. In inert atmosphere, it directly comes into metallic state, which is the active phase of both metals in ESR reaction [248].

3.2.2 Catalyst activity test

The Catalyst activity was performed at atmospheric pressure in vertical fixed bed tubular quartz reactor, having inner diameter 9mm equipped and with a preheater. The ethanol and water having molar ratio 1:3 was fed into preheater region at the rate of 4ml/h with the help of a syringe pump. The catalyst bed was prepared by placing 100 mg of catalyst over quartz wool base at the centre of the reactor. The inert atmosphere in the

reactor was provided by flushing with argon gas initially, and then temperature was increased up to 573K. Before performing the reaction, $NiCo_2O_4$ was pre-reduced to make it active for ESR. The Ni and Co catalysts were used separately to carry out the reaction because these are active phases to perform the reaction.

3.3 Results and discussion

3.3.1 Characterization studies

3.3.1.1 Textural characterization

The surface area of Co, Ni and $NiCo_2O_4$ was determined and was found to be 3.89 m^2/g, 16.67 m^2/g and 95.51 m^2/g respectively. The high surface area of $NiCo_2O_4$ in comparison to Co and Ni was due to higher thermal stability of the spinel catalyst in comparison to elemental Co and Ni obtained as result of thermal decomposition of their oxalates. The high surface area of catalyst may facilitate the ethanol conversion but the selectivity of produced gas is governed by the nature of the catalyst.

3.3.1.2 XRD analysis

The X-Ray diffraction patterns of Co, Ni and $NiCo_2O_4$ are represented in Figure 3.1. The XRD pattern of cobalt showed the major peaks of Co^0 and minor peaks of CoO states. While, in case of nickel, only Ni^0 state was observed. The face centred cubic phase of Ni at 2θ value 45.50°, 53.04° and 78.32° were matched with JCPDS (88-2326). The 2θ value 44.20°, 51.53° and 75.87° correspond with cubic and face-centered crystallite of Co, JCPDS (89-4307). Although, the 2θ value 36.47°, 42.41°, 61.47°, 73.62°and 77.49° were found corresponding to JCPDS (71-1178) of CoO. The peaks of $NiCo_2O_4$ were found at 2θ values of 31.15°, 36.70°, 44.83°, 59.13° and 64.97° are in according to JCPDS (73-1702). The $NiCo_2O_4$ XRD pattern has shown spinel form of nickel and cobalt.
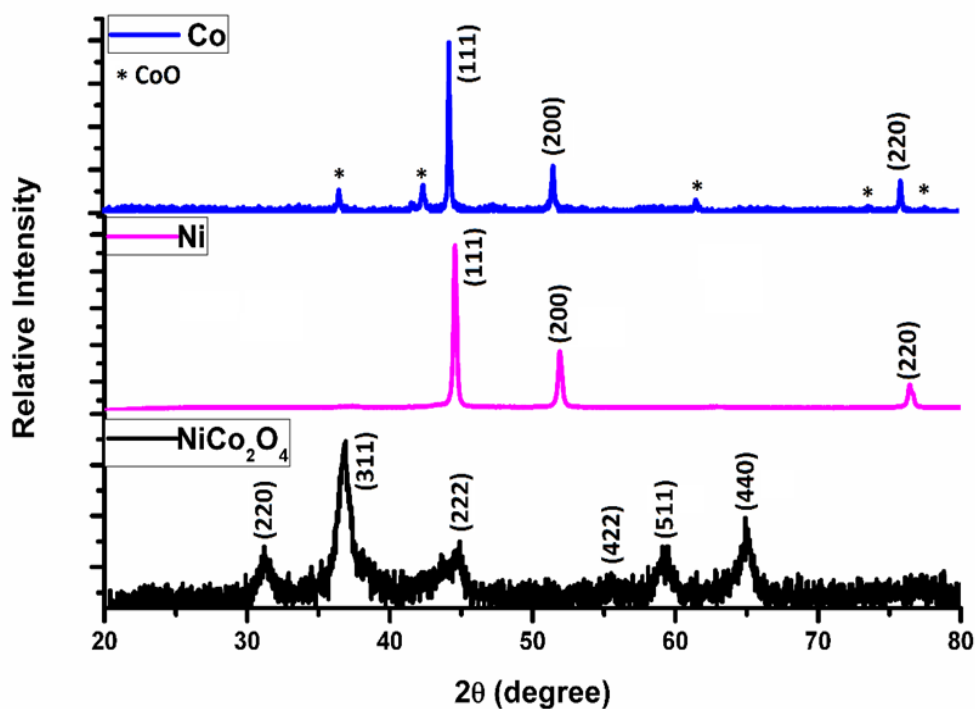
Figure 3.1 XRD pattern of Co, Ni and NiCo$_2$O$_4$ catalysts

The crystallite size of Co, Ni and NiCo$_2$O$_4$ calculated from XRD data by Debye-Scherrer equation were found to be 40 nm, 30 nm and 7.3 nm respectively.

3.3.1.3 XPS analysis

The XPS analysis was performed for NiCo$_2$O$_4$, and peak deconvolution for Co, Ni and O are presented in Figure 3.2. The XPS data deconvolution revealed several peaks for Co and Ni including satellite peaks. The peak at binding energy 780.1 eV and 781.3 eV could be assigned for 2p$_{3/2}$ Co$_3$O$_4$ and Co$_2$O$_3$ respectively. The binding energy at 795 eV and 797 eV could be allocated for Co$_3$O$_4$ and Co$_2$O$_3$ of 2p$_{1/2}$, whereas the region between 785 - 793eV could be assigned for satellite peaks of different states of Co in the
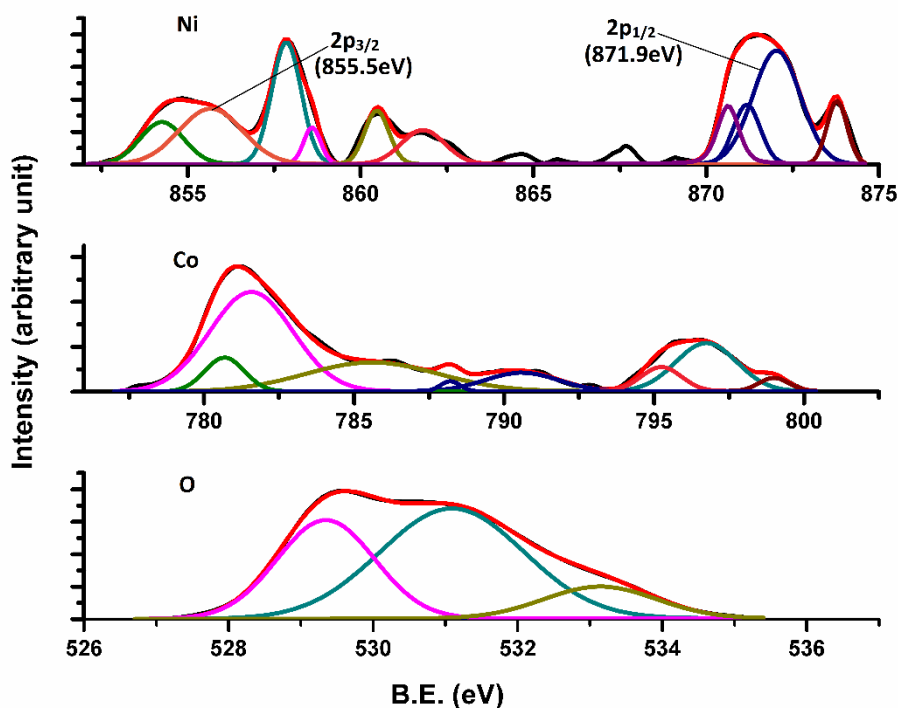
Figure 3.2 XPS peak de-convolution of Ni, Co and O for $NiCo_2O_4$.

Co_3O_4 and Co_2O_3 respectively. It is obvious because small amount of Co_3O_4 was confirmed by XRD and XPS graph analysis and Co existed in two different states in its Co_3O_4 form.

The $2p_{1/2}$ peak of NiO was found at binding energy of 871.9 eV and 873.8 eV. The peaks having binding energy 870 eV and 872 eV could be assigned for CoNi $2p_{1/2}$, which was possible due to spinel form of $NiCo_2O_4$. The peak at 853 eV could be allocated for CoNi $2p_{3/2}$ and 855.5 eV and 857.2 eV for NiO. These binding energy values were in agreement with NIST XPS database. The peaks of Ni $2p_{1/2}$ and $2p_{3/2}$ at binding energy 871.9 eV and 855.5 eV could be assigned for NiO at the octahedral site of spinel structure of $NiCo_2O_4$ [249, 250]. The spinel form of Co and presence of Ni at octahedral site of spinel confirmed the spinel form of Ni and Co which was in agreement with the XRD of spinel form of $NiCo_2O_4$.

The oxygen deconvoluted peaks at binding energy 529.3 eV, 531.0 eV and 533.1eV could be assigned to metal–oxygen bond, oxygen ion at low coordination at the surface and physisorbed water at the surface respectively [33].

3.3.1.4 Morphology analysis

The SEM images of fresh and spent catalysts are presented in Figure 3.3. The particle size calculated from TEM image, with the help of image J software. The particle size of Co (Figure 3.3a), Ni (Figure 3.3b) and $NiCo_2O_4$ (Figure 3.3c) were found 50-60 nm, 40-50 nm and 10-15 nm respectively. The particle size of Ni, Co and $NiCo_2O_4$ were found to be higher than the crystallite size obtained from XRD which is possible due to agglomeration of particles by thermal calcination.
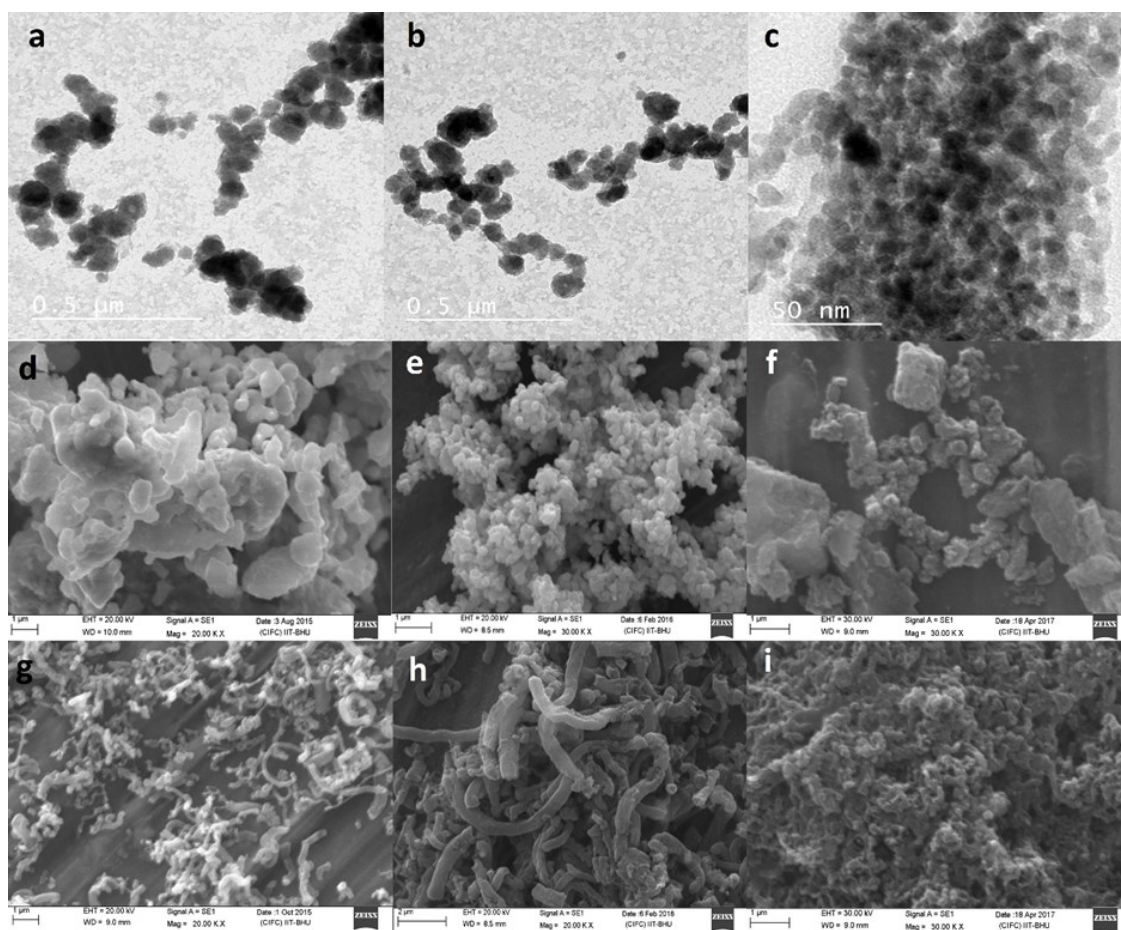

Figure 3.3 TEM (a, b and c), SEM images of fresh (d, e and f) and used (g, h and i) catalysts for Co, Ni, and $NiCo_2O_4$ respectively.

The interesting point for spent catalyst was regulating the diameter of carbon filament obtained form after the reaction. The fresh catalyst of Co has relatively larger size than Ni, but the carbon filament form obtained after reaction was found to have relatively less diameter (20-25nm) than the carbon filament form with Ni catalyst (50-60 nm). In case of $NiCo_2O_4$, mixture of both nano-filament having diameter 15-25 nm can be seen (Figure 3.3f), which forms lumps of carbon filament. It indicates that presence of Co with Ni leads to formation of less thick carbon nano-filament during ESR.

3.3.2 Ethanol steam reforming study

The blank test data suggest that maximum 20% ethanol conversion is possible at 873K in the presence of quartz wool (Figure 3.4). It indicates that quartz wool is inert for ESR reactions and so thus can be used for bed preparation. The outlet gas contains H_2, CO, CO_2, CH_4 and C_2H_4 indicating thermal decomposition of ethanol occurred primarily.
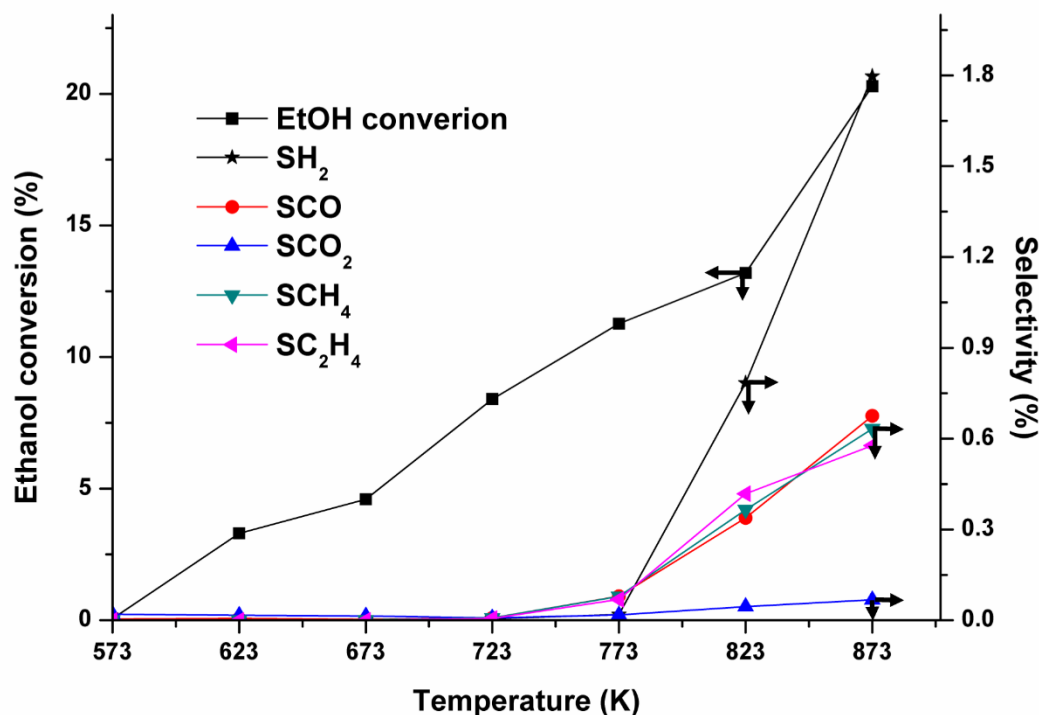

Figure 3.4 Conversion of ethanol and selectivity of produced gases with temperature in the absence of catalyst.

The presence of trace amount of C_2H_4 in outlet gas also indicates dehydration of ethanol due to presence of quartz wool.
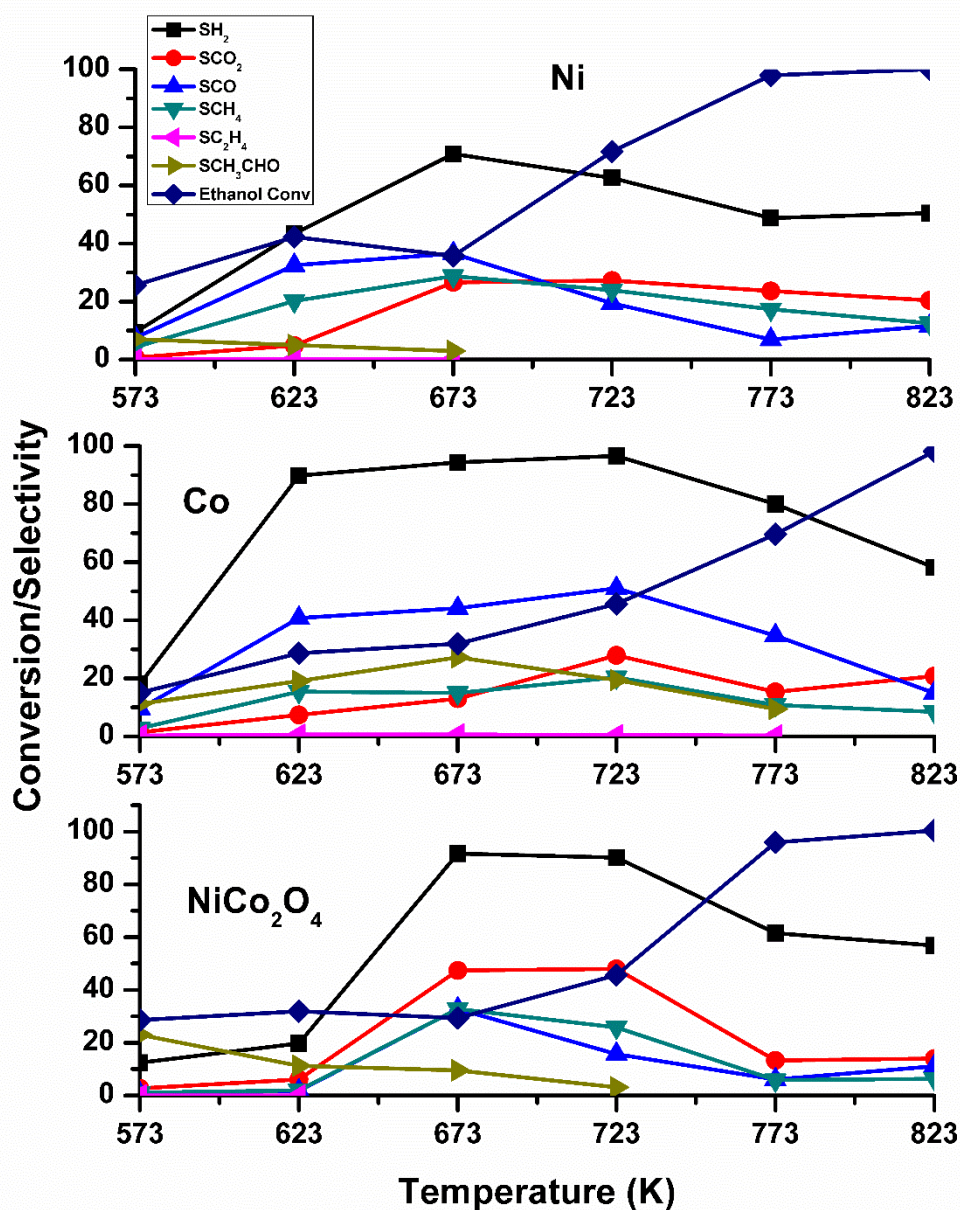

Figure 3.5 Catalyst activity and selectivity of Ni, Co and $NiCo_2O_4$ for ESR (molar ratio of $H_2O:C_2H_5OH = 3:1$, WHSV= 35.4h^{-1}).

Figure 3.5 represents selectivity of different gases generated and ethanol conversion with temperature. It is evident from the figure that with an increase in temperature, ethanol conversion increases, but the selectivity of different gases varies abnormally with temperature. It may happen because of the that at dissimilar temperature, the feasibility of various reactions is different and the presence of a different kind of catalyst also affects the reaction pathways.

In case of Ni, the selectivity of CO is higher than CO_2 at lower temperature (573K and 623K) but with increase in temperature selectivity of CO_2 increased and selectivity of CO got decreased. The hydrogen selectivity was gradually increases upto 723K, but later on (after 723K) it declines abruptly. Thus, product gas distribution suggested that ethanol decomposition prominently occurred at lower temperature. However, the outlet liquid mixture also contained acetaldehyde at 573K-673K in trace amount.

It indicates that at lower temperature dehydrogenation reactions are also possible with Ni catalyst. At lower temperature, the CH_4, CO_2 and H_2 selectivity increases, whereas at higher temperature their selectivity is almost constant. These variation in selectivity of different gas suggest that the following reactions may be dominant reactions during ESR with Ni catalyst [251, 252] :

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3.1}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{3.2}$$

In case of cobalt catalyst, the selectivity of CH_3CHO was significant. However, their selectivity decreases with increase in temperature due to decomposition at higher temperature but it was present within temperature range 573K-773K. It indicates that the cobalt is actively participating in dehydrogenation reaction followed by decomposition of acetaldehyde into CO and CH_4. It has similar product distribution as obtained from

ethanol decomposition reaction (eq1.5) but significant acetaldehyde concentration confirms dehydrogenation pathways (eq1.3), and with temperature, the different paths lead to dissimilar product selectivity.

The CO selectivity for Co was more than double of CH_4 selectivity and it maintains almost constant ratio at each temperature. It indicates that Co followed the hydrogenolysis pathway (eq1.7) of ethanol and hydration (eq1.18) or dry reforming (eq3.2) of CH_4 leads to higher CO formation than CH_4. In the case of Ni, the CO selectivity was found to be higher than CH_4 up to 673K, and it got lowered above temperature 723K. Behaviour of both the catalysts for CO and CH_4 selectivity indicated that dehydrogenation and hydrogenolysis reactions had prominently occurred with Co but in case of Ni, decomposition reactions of ethanol occurred significantly.

The ethanol conversion was almost comparable upto 723K for each catalyst. At 773K, ethanol conversion was lowest for Co catalyst, but hydrogen selectivity (80%) was higher than Ni. The hydrogen selectivity of $NiCo_2O_4$ at 773K is higher than Ni and lower than Co but the ethanol conversion was greater than Co and comparable to Ni. It indicates that the bimetallic spinel state of Ni and Co had synergistic property regarding ethanol conversion and hydrogen selectivity.

The C_2H_4 formation was found noticeable at temperature 773K and 673K for Co and NiO respectively, whereas, it was found until 623K for $NiCo_2O_4$. The acetaldehyde formation persisted until 773K, 673K and 723K for Co, Ni and $NiCo_2O_4$ respectively. It indicates that acetaldehyde decomposition started at 673K with Ni but even in presence of Co, Ni can initiate the acetaldehyde decomposition at 723K. The product gas selectivity of C_2H_4 and CH_3CHO revealed that bimetallic interaction significantly reduced the dehydration and dehydrogenation reaction during ESR with temperature.

The cobalt catalyst followed dehydrogenation and hydrogenolysis of ethanol, whereas Ni follows the decomposition of ethanol pathways. Therefore, ethanol conversion mostly occurred in case of Ni, but the selectivity of H_2 was found higher for Co, whereas, $NiCo_2O_4$ can be considered as optimum behaviour for ethanol conversion and hydrogen selectivity.

3.4 Conclusion

Ni and Co were the active metals for ESR, but their oxides need to be reduced to produce active phases. However, it was found that the active phases can be directly formed by thermal decomposition of their oxalate precursors. The ethanol conversion over $NiCo_2O_4$ is lower than Ni but higher than Co. Whereas, H_2 selectivity for $NiCo_2O_4$ catalyst is higher than Ni but lower than Co. It was found that the $NiCo_2O_4$ spinel has better performance for hydrogen generation than Ni and Co.