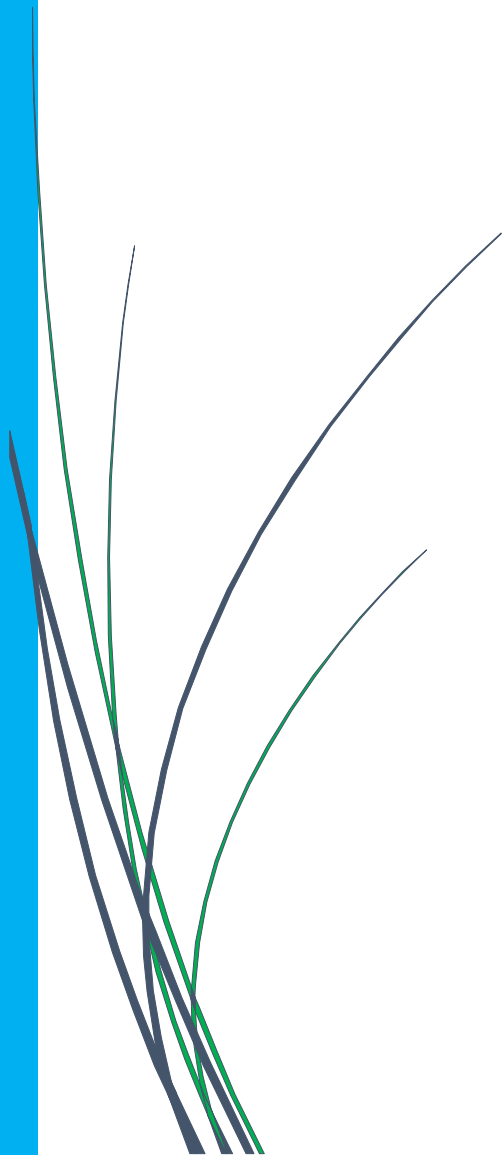




Chapter:6

**ZSM-5 supported
Co versus Ni
catalysts for ESR**



6.1 Introduction

The ethanol steam reforming requires an active low-cost catalyst to make it sustainable [307, 308]. The solid heterogeneous catalysts are stable at higher temperatures [309]. The study over Al_2O_3 , SiO_2 , CeO_2 , ZrO_2 , MgO and their mixed oxides as a support have been reported for ESR with diverse kind of active noble as well as non-noble metals. [151, 157, 176, 223, 239, 253, 310-312] The special structural catalyst such as perovskite, hydrotalcite, and spinel were also reported [47, 72, 145, 198, 241, 242, 265, 313, 314]. However, Na-Y Zeolite support with Rh, Co and Ni-based catalyst were studied by few authors [315-318].

Zeolite group can be used as sustainable support because of high surface area and porosity. Modulating the electronic properties of active sites and molecular dimension of pores are also two advantageous characteristics. Among different types of zeolite, ZSM-5 had been classified as medium pore zeolite having ten oxygen atoms in the open ring [319]. Their constituent oxides (Al_2O_3 and SiO_2) are economical than other active noble metal supports (CeO_2 and ZrO_2). ESR is the temperature dependent process for the desired selectivity of gases. Therefore, one of the most advantageous characteristics is their temperature sustainability with variation in SiO_2 and Al_2O_3 concentrations. The Si-O bond is more stable than Al-O bond and therefore high temperature ESR could be sustainable at higher SiO_2 concentration. Inokawa et al. [316] have examined the effect of preparation methods and the role of basicity with Co and Ni based catalysts. They found that the catalyst prepared by ion exchanged were produced hydrogen via dehydration of ethanol whereas, impregnation method used for catalyst preparation had shown hydrogen production by dehydrogenation of ethanol. In this study, ZSM-5 was taken as support having Si:Al ratio 50:1, for high temperature ESR and impregnation method was used to prepare the catalyst. Among, non-noble active metals, Co and Ni

based catalysts have shown considerable activity with diverse supports during ESR. Their catalytic activity is highly governed by the type of support used during ESR. Considering all of aforementioned points and absence of study with both of the active metals (Co and Ni) with ZSM-5, the catalytic properties of Co/ZSM and Ni/ZSM for ESR were studied at high temperature.

6.2 Experimental

6.2.1 Catalyst preparation

All the analytical grade chemicals were used in the preparation of catalysts like, ZSM-5 ($\text{Al}_2\text{O}_3:\text{SiO}_2$ molar ratio 1:50), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Alfa Aesar. 10% Co/ZSM and 10% Ni/ZSM were prepared through wet impregnation method at room temperature as reported by Inokawa et al. [316] over ion exchange method. Ethanol was used for impregnation medium and agitation was done for 6h for preparation of both catalysts. After impregnation, it was kept in oven to dry overnight at 353K. Then dried mixtures (Co/ZSM and Ni/ZSM) were calcined at 973K for 4h.

6.2.2 Catalytic performance tests

The performance tests were carried out into a fixed bed quartz tubular reactor as described in chapter 5. Prior to perform the reactions, the catalyst was pre-reduced *in situ* with pure H_2 flowing at the rate of 20ml/min and at temperature 873K for 1h. After pre-reduction of catalyst, argon gas was flushed to remove hydrogen molecules over the catalyst bed. The syringe pump was used to feed the ethanol water mixture (3:1 molar ratio) into the preheater (453K) at WHSV of 35.4h^{-1} . To create the inert atmosphere, He (99.99% purity) was passed with the flow rate of 10ml/min. The experiments were performed from 723K- 973K at the interval of 50 K with fresh catalyst sample. The product distribution data were recorded after stabilization period of 1h at particular

temperature. The Time on stream study was performed with fresh catalyst at optimum temperature for 6h.

6.3 Results and discussion

6.3.1 Characterization studies

6.3.1.1 Textural analysis

The surface area and pore volume were mentioned in Table 1 indicating decrease in surface area as well as pore volume by impregnation of Co and Ni. It might have happened by occupying the pores of ZSM-5 by active metals.

Table 6.1 Surface area and pore volume of catalyst

Sample	Surface area (m ² /g)	Pore volume (ml/g)
ZSM-5	440.0	0.280
Co/ZSM-5	330.7	0.131
Ni/ZSM-5	343.5	0.193

6.3.1.2 XRD analysis

The HR-XRD profile of ZSM-5, Co/ZSM-5 and Ni/ZSM-5 had shown in Figure 6.1. Three consecutive high intensity peaks of ZSM-5 having specific 2θ value 22° - 24° were commonly found in each catalyst. The two consecutive peaks at 44.9° and 45.4° were also commonly observed in each sample. It indicates that after calcination, ZSM-5 structure was retained in both of the catalysts. The 2θ values of Co_3O_4 in Co/ZSM-5 were found at 38.5° , 65.2° and 77.3° . These values were in agreement with JCPDS (43-1003). The peaks of NiO in Ni/ZSM-5 can be observed at 2θ value 43.2° , 75.3° , 79.2° and these were matched with JCPDS (65-6920). Therefore, the XRD analysis suggests that spinel phase of Co and NiO form of Ni was formed after calcination.

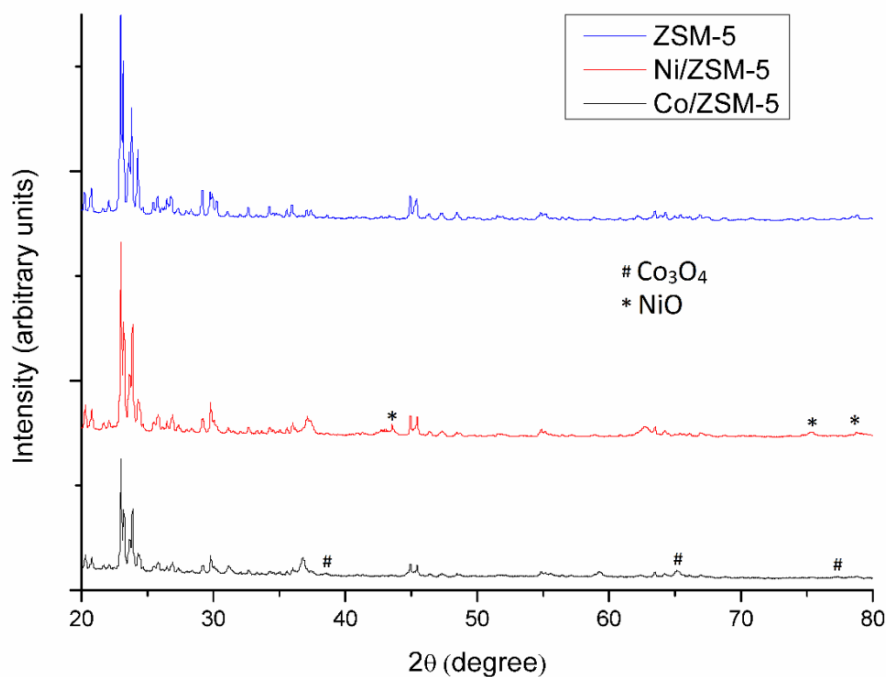


Figure 6.1 HR-XRD of ZSM-5, Ni/ZSM-5 and Co/ZSM-5.

6.3.1.3 FTIR analysis

The FTIR spectra has been presented for ZSM-5, Co/ZSM-5 and Ni/ZSM-5 fresh as well as spent catalysts (Figure 6.2). The transmittance in between $3700\text{-}3600\text{cm}^{-1}$ was of low intensity. But an acidic bridging hydroxyl stretching region was found in ZSM-5 at 3610 cm^{-1} which became very weak after the exchange of active metal ions. The weak band near 3745 cm^{-1} was due to isolate and terminal silanol groups. Whereas, the shoulder peak near 3640 cm^{-1} was due to internal silanol groups and 3665 cm^{-1} was due to Al-OH species. [320, 321] The weak band near 1220cm^{-1} represented asymmetrical T-O-T stretching. It is also considered an indicative of heteroatom substitution and so this peak intensity was relatively higher for pure ZSM [322]. Transmittance near 1080 cm^{-1} and 793 cm^{-1} can be attributed to Silica which was assigned to internal vibration of Si, AlO_4 tetrahedra. Whereas, 550 cm^{-1} was assigned to double ring of tetrahedra in zeolitic framework [323].

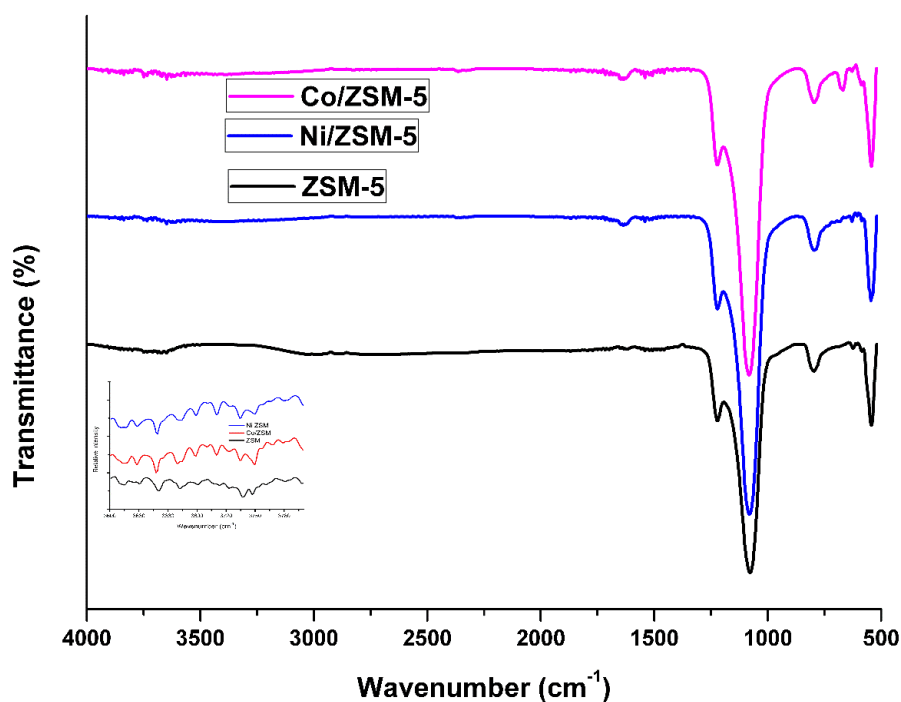


Figure 6.2 ATR- FTIR of fresh as well as spent catalysts.

It is clear from the Figure 6.2 that the weak peak of NiO at 650 cm^{-1} and strong peak of Co_3O_4 at 562 cm^{-1} get overlapped with ZSM-5 peaks [324]. The peak of Co_3O_4 and NiO is also in agreement with HR-XRD study of Co/ZSM-5 and Ni/ZSM-5 catalyst. It was also in agreement with HRXRD study of Co/ZSM-5 catalyst.

6.3.1.4 TPR analysis

Figure 6.3 represents Temperature program reduction profile of Co/ZSM-5 and Ni/ZSM-5. Ni /ZSM-5 has shown single peak at 650 K which can be considered for the reduction of NiO species. Moreover, Co/ZSM-5 has two characteristic peaks at 628K and 738K. It may be due to two different reduction states of Co_3O_4 state which was in agreement with both of the HR-XRD and FTIR data of catalysts. The reduction of Co_3O_4 into CoO and CoO to Co^0 states can be assigned at temperature 628K and 738K respectively [132]. The Peak at 738K can also be considered due to reduction of Co-oxo

ions, may be formed by the reaction of Co with available protons in zeolite during calcination [320].

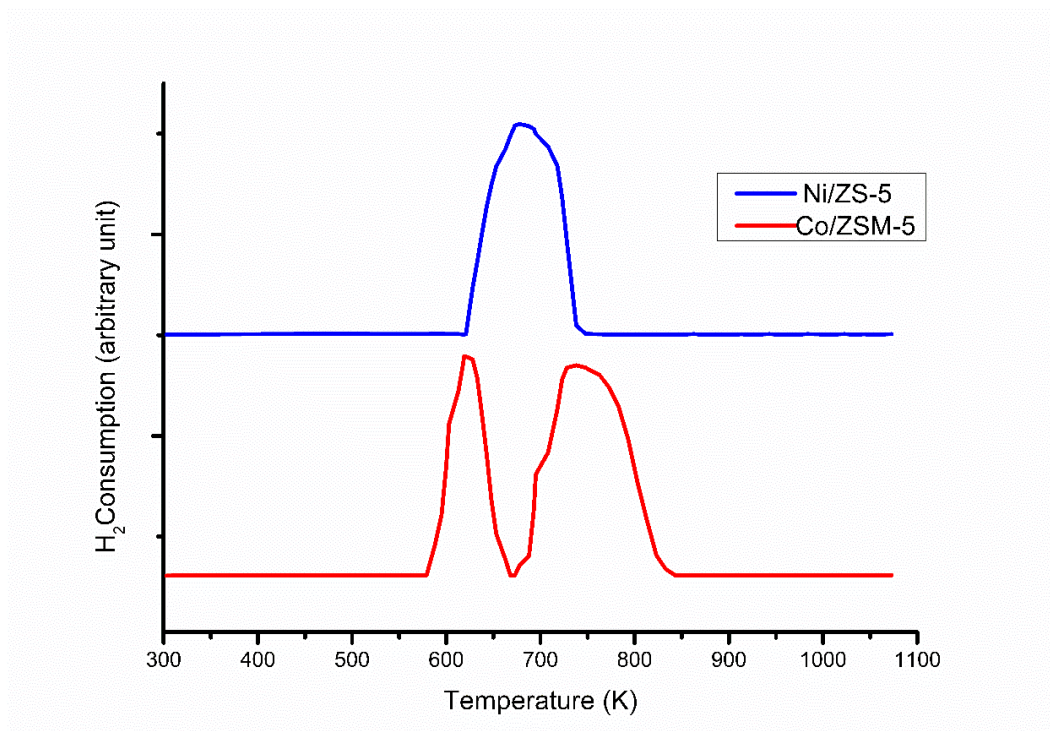


Figure 6.3 H₂-TPR profile of Co/ZSM-5 and Ni/ZSM-5.

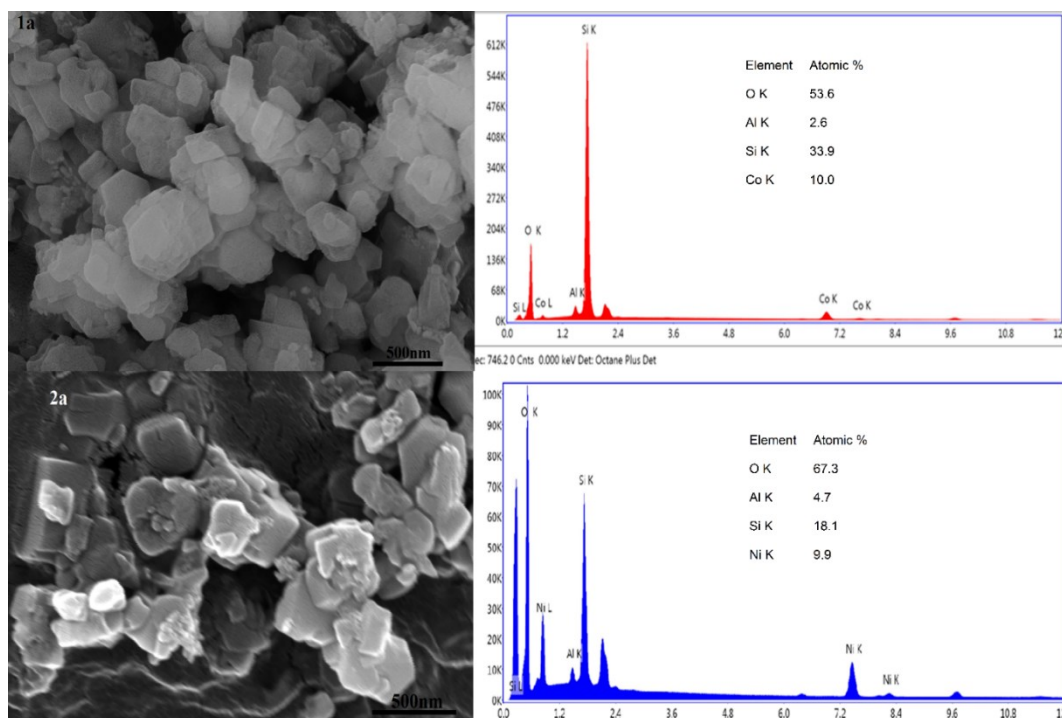


Figure 6.4 HR-SEM and EDAX of Co/ZSM-5 (1a) and Ni/ZSM-5(2a).

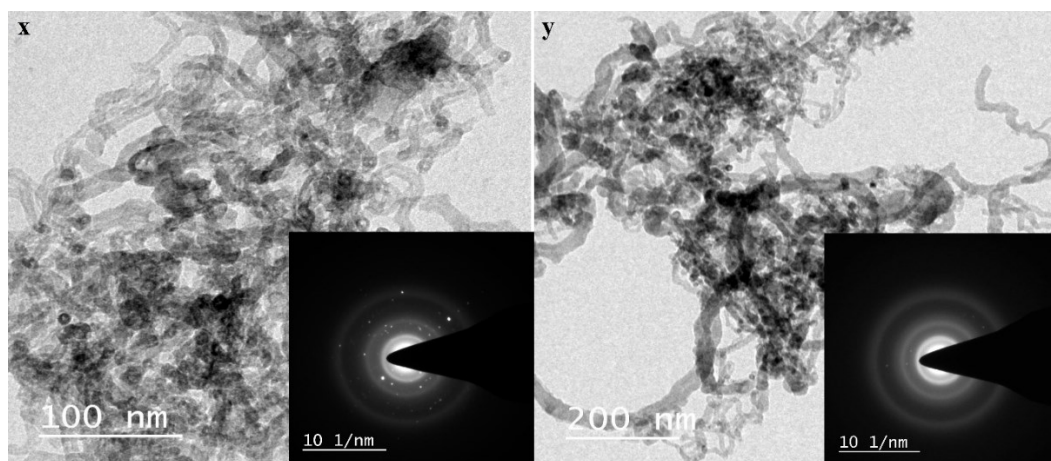


Figure 6.5 TEM and SAED images of spent Co/ZSM-5 (x) and Ni/ZSM-5 (y).

6.3.1.5 Morphology analysis

Figure 6.4 represents the HR-SEM with EDAX images of fresh catalysts. In Figure 6.4 1a and 2a HR-SEM and EDAX of fresh catalyst of Co/ZSM-5 and Ni/ZSM-5 were presented. The EDAX data suggest the loading of active metals are common for both the catalysts. The particle size calculated from image J software were found 300-360 nm for Ni/ZSM-5 as well as Co/ZSM-5. The TEM analysis of spent catalysts reveals abundant growth of filamentous carbon formation over spent catalysts. The diameter of filamentous carbon was observed to be 9nm-30nm for both the spent catalysts. Growth of these filaments from common points like octopus can also be observed from Figure 6.5x (spent Co/ZSM-5) and 6.5y (spent Ni/ZSM-5). The SAED pattern for both of the spent catalyst had shown ring like pattern due to profusion of carbon filaments. The halo around bright centre spot indicates amorphous nature of carbon.

6.3.2 ESR performance test

The ESR performance over ZSM-5 has shown maximum ethanol conversion 23.7% at 923K with lower H₂, CO, CH₄, CO₂ and abundant higher hydrocarbon (C₂H₄ and C₂H₆) generation. It can be considered due to dehydration and polymerization of coke and their hydration reaction. Figure 6.6 represents the ethanol conversion and selectivity of major gases with variation of temperature for Co/ZSM-5. After 873K, double carbon

containing hydrocarbons were absent but ethyl acetate formation was started prominently at 923K. The C_2H_4 formation was most prominent at 723-823K but it completely disappears at temperature 923K. The trace amount of acetaldehyde was also obtained at temperature 723K to 873K. However, the ethanol conversion was about to complete (97.4%) at 773K but hydrogen selectivity was achieved highest at 923K. The selectivity of CO_2 increases at the cost of C_2H_4 selectivity at 773K, whereas the C_2H_4 as well as CH_4 selectivity was reduced and CO_2 selectivity increased at 823K. The absence of C_2H_4 in the generated gas at 923K and increase of CO formation as well as CH_4 formation indicates C_2H_4 decomposition accompanied with carbon hydration (eq1.15) prominently rather than carbon hydrogenation (eq1.13).

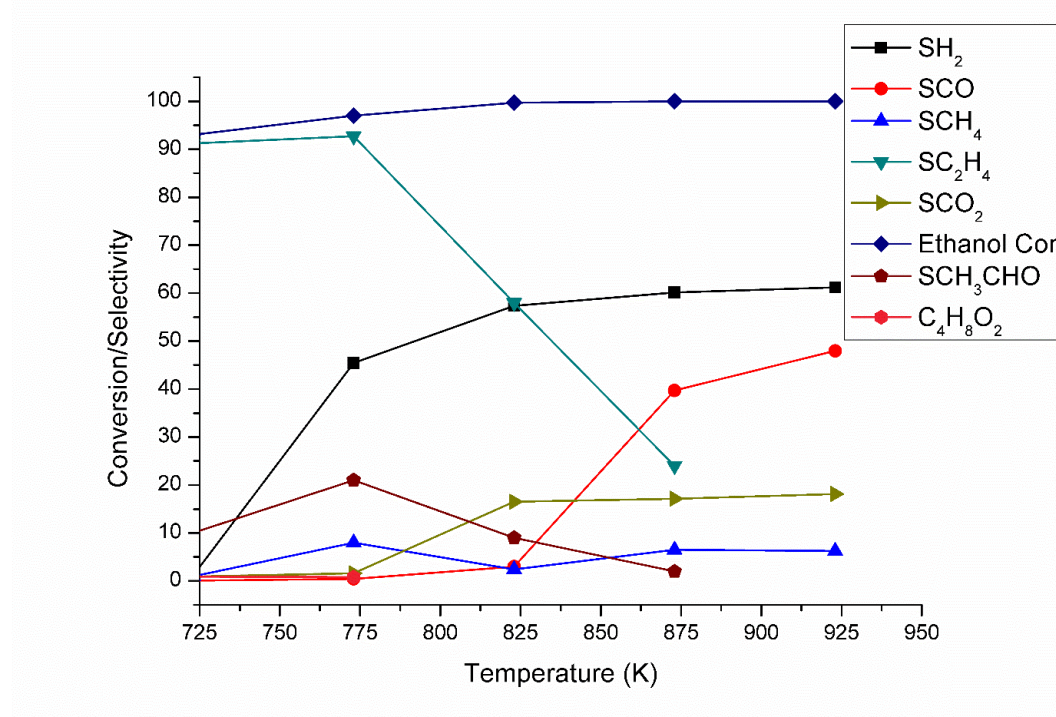


Figure 6.6 The conversion of ethanol and selectivity of abundant gases with temperature over Co/ZSM-5.

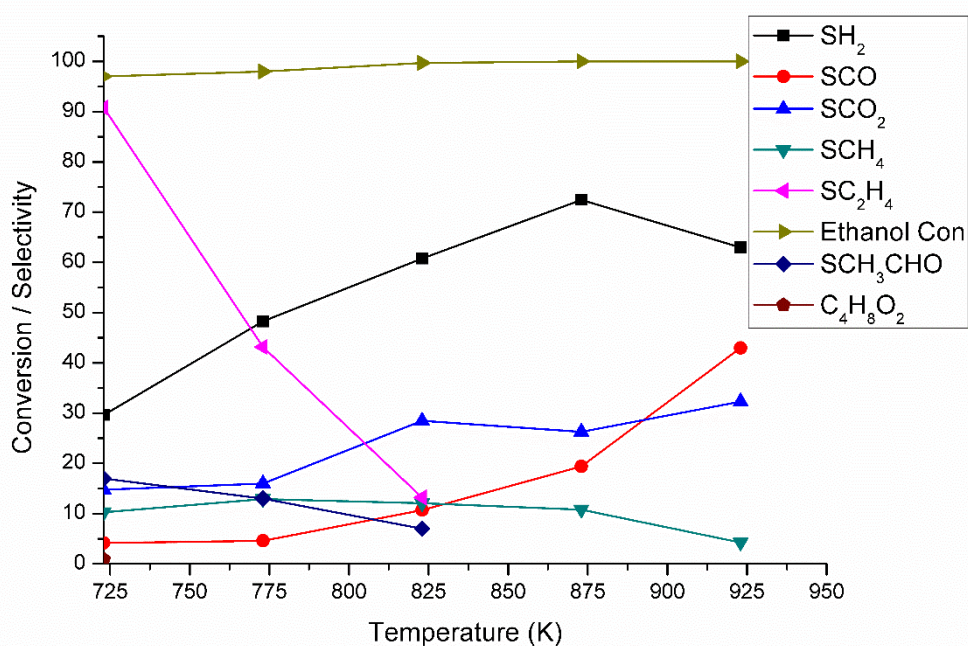


Figure 6.7 The conversion of ethanol and selectivity of abundant gases with temperature over Ni/ZSM-5.

Figure 6.7 represents the ESR performance within 723K- 923K temperature range for Ni/ZSM-5. The ethanol conversion was about to complete (98.5%) at 773K but the selectivity of hydrogen was highest at 873K. The acetaldehyde selectivity was also very less at temperatures 773K and 823K. Hence, in terms of relative temperature for hydrogen selectivity and ethanol conversion, Ni has shown better activity as compared to Co. The CH₄ and CO selectivity were also increased by reducing C₂H₄ selectivity, but were lesser as comparative to H₂ and CO₂ selectivity increment. Hence desired gas composition is higher for Ni based catalyst relative to Co. The selectivity of C₂H₄ was observed up to temperature 873K for Co/ZSM-5, whereas, only up to 823K for Ni/ZSM-5. The C₂H₄ generation was commonly generated up to certain temperature range for both of the catalysts indicating acidic nature of ZSM-5. Since, the used zeolite support was NH₄ ZSM-5 and the NH₄ balancing the acidity of zeolite released out as NH₃ gas on calcination (773K).

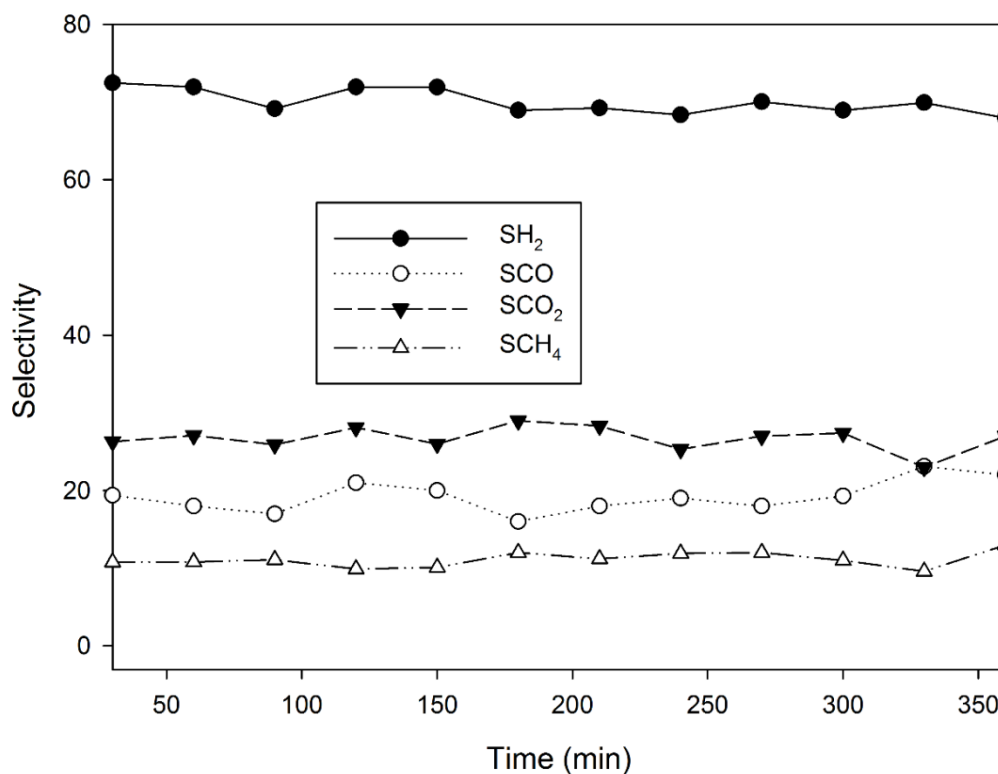


Figure 6.8 Performance stability with 6h time on stream study at temperature 873K for Ni/ZSM-5.

The time on stream study was performed for Ni/ZSM-5 at temperature 873K as presented in Figure 6.8. It shows product distribution nearly constant for 6h. However, the spent catalyst has shown considerable carbon deposition on the surface of catalysts. The amount of carbon was found to be 23.3% of Ni/ZSM-5 catalyst mass.

6.4 Conclusion

The Ni/ZSM-5 catalyst has shown lower C₂H₄ and higher H₂ selectivity as compared to Co/ZSM-5. The temperature was also found lower for Ni/ZSM-5 in terms of ethanol complete conversion and hydrogen selectivity. It indicates that Ni is more active for scission of C-C bond at lower temperature with ZSM-5 support as compared to Co.