Chapter-4 : TRANSFORMATION OF STYRENE OXIDE ON SUPPORTED Co, Ni and Cu CATALYSTS

Abstract

Bifunctional supported metal catalysts with Co, Ni and Cu (as active metals) supported on bicomponent zirconia-alumina supports prepared by deposition – precipitation are studied for the transformation of styrene oxide.

Effect of zirconia content which affects characteristics of these catalysts such as acidity, XRD crystallite size, MSI (metal support interactions), preferential orientation of crystal planes and surface concentration of active metals (XPS) (as covered in chapter 3) are correlated with activity, product selectivity and stability of these catalysts for transformation of styrene oxide.

The effect of difference between electronic properties of Cu relative to those of Co and Ni is also examined for correlation with differences in performance of the catalysts for this reaction.

4.1 Introduction

Styrene oxide (SO) can be hydrogenated to 2-phenylethanol (2-PEA). Styrene oxide can also be isomerized to phenylacetaldehyde (PAA). Both these products are important perfumery chemicals in the fragrance industry and in the flavor industry. 2-PEA has fragrance and flavor of rose petals because of which it is used in perfumes, deodorants, soaps etc. It has antibacterial and antifungal activity because of which it is used in antiseptic creams. It is also used in shampoos and hair dyes to improve texture of hair[1]. It also has local anesthetic properties. It is an important chemical intermediate and is used in preparation of styrene, phenyl acetaldehyde, phenyl ethyl ester, phenylacetic and benzoic acids and bis-phenyl ether.

The fragrance of PAA is described as “green floral odour” with a honey-like flavor. PAA is an intermediate for preparing active ingredients for insecticides, as an agent to control rate of polymerization in manufacture of polyesters, as a fragrance / flavor chemical in flavored cigarettes.

The former reaction mentioned above, which constitutes hydrogenation is a metal catalyzed reaction whereas the latter is an acid catalyzed reaction. PAA can be produced by various routes[2] such as dehydrogenation of phenylethanol, isomerization of SO, from alkyl or alkoxy substituted SO using a Ti based zeolite, rearrangement of styrene glycols over aluminosilicates, Rosenmund reduction of carbonyl chlorides. Isomerization of SO to PAA over phosphotungstic heteropoly acid in cyclohexane [3], acid catalysts such as zeolites, Nafion[4] or heteropoly acids[3] are reported for preparing phenyl acetaldehyde.

A number of optional routes are available for preparation of 2-PEA. 2-PEA can be prepared from alkylation of benzene with ethylene oxide through Friedel Crafts reaction[5]. Use of $AlCl_3$ and formation of dibenzyl coproduct are disadvantages. Or through Grignard synthesis, conversion of chlorobenzene to phenyl magnesium chloride followed by reaction with ethylene oxide to form phenylethoxymagnesium chloride. Decomposition of the latter with H_2SO_4 yields 2-PEA. The coproduction of biphenyl as by-product affects its use as perfumery chemical[6]. Hydrogenation of styrene oxide is another route to 2-PEA. Hydride based reductants such as $NaBH_4$, $LiAlH_4$, B_2H_6 etc. are used[7].

A variety of heterogeneous catalysts are reported for this reaction. Noble metals such as supported Pd or Pt are reported. Bajaj et.al[8] teach the use of Pd(II) salt supported on basic supports such as MgO or hydrotalcite as well as basic alumina, Na-beta zeolite and carbon in batch reaction. 100 mg NaOH is added to all reaction tests. They report complete conversion with selectivity between 98-98.5% at 30°C, 500psig, 3h batch time for catalysts with 5 wt% Pd. High Pd content and the need for addition of NaOH are disadvantages.

Kirm et.al.[9] have studied Pd supported on AC (activated carbon), MgO and alumina for hydrogenation of styrene oxide in continuous flow reactor. They report conversion 98.0% with 99.5% selectivity to 2-PEA for 2% Pd/MgO, 99.5% conversion with selectivity of 8.5% to 2-PEA, 56% to 1-PEA and 35.5% to PAA for 2% Pd/Al_2O_3 and 99.8% conversion with selectivity of 32% to 2-PEA, 3% to 1-PEA and 65% to PAA for 2% Pd/AC at 348°C, 10000 $h^{-1.}$ Substituting Pd with 2% Pt [10] gives 99.8% conversion with selectivity 94.6% (2-PEA), 5.4 (PAA) on MgO, conversion 95%, selectivity's 3.9% (2-PEA), 36.2% (1-PEA), 56.1% PAA, 3.8% to other products on alumina, and conversion 99.7% with selectivity 78.3% (2-PEA), 2.8% (1-PEA), 18.9% (PAA) on AC at 348°C, 10000h^{-1}. Indicating that support with basic character gives better results.

Patent by Hoelderich et.al[11] shows use of 3.4% Cu or 0.5-0.95% Pd/zeolite catalysts for hydrogenation of SO in vapor phase at 250-300°C with space velocity of 1.5-3.0 h^{-1} (on SO). They report 100% conversions and 34-84% selectivity to 2-PEA at 250 °C for various catalysts. 23-49% PAA formation at 300°C on Cu based catalysts. Formation of by-products such as styrene, EB, toluene and xylene up to 20-30% (cumulative) is also reported by them. Comparing results of

Kirm et.al.[9][10] and Hoelderich et.al.[11] it is clear that noble metals have an activity advantage (high conversion and selectivity at high space velocity) provided noble metal content is in the percentage range.

Majority of studies are in batch mode with use of organic solvents. Batch time ranges from 1-5h [12][13][14][15][16]. Disadvantages therein are low productivity and cost incurred in separating the catalyst and recovering the solvent from the product mixture.

Use of Raney nickel (bulk metal)[17][18][19], Chandalia et. al.[19] results in 92% conversion with 90.2% selectivity to 2-PEA in batch reactions. Gibson et.al.[18] reported use of Raney Nickel with IPA as solvent for liquid phase hydrogenation of SO in batch reactors. An alkaline medium is maintained by adding soda ash. SO is continuously fed over 5 hours duration with additional hour for completion of reaction. Yield of 95.5% is reported.

Supported non-noble metals, Ni, Co and Cu supported on various refractory supports[13][14][15][16][20][21] [22][23] are reported in literature and patents. Sasu et.al[13] have studied Ni and Co supported on Mg-Al hydrotalcites prepared by coprecipitation for batch reaction of styrene oxide and PAA. They report SO conversion 84-98% with 68-95% selectivity to 2-PEA, balance EB for Ni based catalysts and 37-98% conversion with 33-41% selectivity to 2-PEA and 58-77% selectivity to styrene for Co based catalyst at different reduction and reaction conditions. They report formation of 2-PEA and oligomers (by aldol condensation) when PAA is used as reactant. Selectivity to 2-PEA increases with temperature of reduction. They report that cascade conversion of SO first to PAA followed by further conversion of PAA to 2-PEA gives high selectivity 98% to 2-PEA. Bergada et.al.[20] have studied physical mixtures of NiO or Ni with MgO and rehydrated MgO for batch conversion of SO. They report near complete selective yield to 2-PEA for mixtures of NiO and MgO followed by reduction with H_2.

Salagre et.al.[16] report Ni nanoparticles supported on saponite prepared by impregnation and ion-exchange. They report conversion 22-100%, 2-PEA selectivity 40%, PAA selectivity 0-72% and also report formation of 2-EPE (2-ethoxy-2-phenylethanol) 28-100% on catalysts prepared by ion exchange. Catalysts prepared by impregnation show conversions 15-55%, 2-PEA selectivity 95-99% and PAA selectivity 5-12% in batch reactions. Poondi et.al[22] report MSI in Pt/TiO_2. This enhances activity 15-20 folds relative to Pt supported on SiO_2 or eta-Al_2O_3 with 70% selectivity to 2-PEA at 60% conversion in hydrogenation of PAA. However, they report a multitude of by-products (Benzene, Toluene, Ethyl Benzene, styrene, cyclohexylethanol, cyclohexylethanal in significant concentrations. Selectivity to 2-PEA improves upon reduction at high temperature (773K). They report formation of Benzene and toluene by hydrogenolysis of PAA.

Psaro et.al.[12] have studied monofunctional and bifunctional catalysts such as SiO_2, SiO_2-Al_2O_3, SiO_2-ZrO_2. 8% Cu loaded on the monofunctional support was studied for batch reaction. They report 26-100% conversion of SO with 65-98% selectivity to PAA on monofunctional catalysts and complete conversion of SO with 8-80% selectivity to 2-PEA, 0-89% selectivity to PAA, up to 7% styrene and 43% EB. They report poor activity of Si-Zr catalysts for isomerization of SO to PAA. Increasing Zr content or decreasing Cu content adversely affects hydrogenation of SO to 2-PEA. Cu/SiZr gives best yield (80%) of 2-PEA but at 5h batch time with dioxane solvent. Poor performance is attributed to penetration of Cu into mesopores of the support. By products such as styrene, EB and C-O coupling dimers are also reported. Solvent used also affects performance. Cu/Si-Zr gave 70% yield in 4.25h in toluene at 90 °C.

The relative distribution of PAA and 2-PEA and the cause of catalyst deactivation in this reaction is attributed to either strong acid sites which leads to coking[23] or basic sites which promote condensation reactions[24]. Weak Lewis acid sites or sites with mild basic character could help in this regard.

The above reports indicate that supports with basic character give better selectivity to 2-PEA, whereas, acidic supports are suited for PAA. However, there is still room for improvement of selectivity. Mostly monocomponent and some bicomponent oxide materials are reported for transformation of styrene oxide. A combination of zirconia-alumina is not reported in literature for this reaction. Also, deposition-precipitation as a method of preparation has not been reported in literature for this reaction. Hence zirconia-alumina composites prepared by deposition-precipitation would make an interesting study.

While batch reactions give high selectivity, productivity is low. Solvents are used which need to be separated in addition to catalyst. This adds to cost.

Commercial catalysts used for producing 2-phenyl ethanol are Pd/C based. The high cost of noble metals is the key driver for development of supported base metal catalysts. The latter are significantly economical than the former (1000 to 4000x cheaper on mole basis)[25].

Patent studies over the period 1910 – 2015, based on database PatBase®, covering over 100 issuing authorities worldwide, indicates significantly more patenting in the area of heterogeneous catalysts for hydrogenation since year 2005. The growth rate of patents based on individual metals as active components for hydrogenation is cited in this study for the period 2011-2015. The growth rate of patents of base metals is higher than that for noble metals such as palladium, ruthenium, rhodium, osmium, iridium or platinum. The growth rates based on patents are shown in parenthesis after each metal: Nickel (7.1%), Copper (4.9%), Cobalt (6.6%) and Iron (9.4%), noble metals as listed above (3.8-4.8%)[26].

Nickel, cobalt, copper and iron exhibit good activity for catalytic hydrogenation. Catalysts based on these metals are widely used for the manufacture of commodity chemicals and purification applications such as synthesis of ammonia, Fischer Tropsch synthesis, substitute natural gas, methanation, saturation of edible oils and fats, hydrodesulfurization, hydrocracking, selective hydrogenation of pyrolysis gasoline etc.[27]. However, noble metals are still widely used in many applications such as manufacture of cyclohexane by the hydrogenation of benzene, selective hydrogenation of acetylene or MAPD (methyl acetylene and propadiene) from C_2 and C_3 hydrocarbon streams, 2nd stage hydrocracking, hydroisomerization of lubes and for the manufacture of specialty chemicals (API's, fragrances and flavors). Hence, there is scope for exploring the use of non-noble metals as catalysts in these areas.

Some interesting differences between Co, Ni and Cu are:

- While all three elements belong to the first transition series, Cu presents an atypical electronic configuration and its Fermi level does not overlap with the d band. Its effect on reactivity is not studied so far for catalytic reactions.
- The Fermi level of Cu does not overlap with the d band of Cu. It is 0.1 eV lower than the d band. Whereas, the d bands of both Ni and Co overlap with the Fermi level[28].
- Quaino et.al.[28] have shown from model Hamiltonian, quantum statistics and DFT calculations, that, an overlap of the d band and the Fermi level is one of three important criteria for good catalytic activity in hydrogen electrocatalysis.
- Co, Ni and Cu belong to the first transition series of the periodic table. The electronic configuration of Cu ($4s^1 3d^{10}$) shows anomalous behavior from that of Co ($4s^2 3d^7$) and Ni ($4s^2 3d^8$) in that, the 3d orbital is completely filled before the 4s orbital (which is half filled).

- The Allen scale electronegativity increases from Sc (1.19) to Co (1.84) and Ni (1.88) and then decreases for Cu (1.85) and Zn (1.59). The Pauling scale also shows a similar trend.
- Cu tends to have I and II (lower) oxidation states, where as Co tends to have II, III, IV, V and Ni II, III, IV (higher) oxidation states. The higher oxidation states are observed in organometallic complexes. Oxides of lower oxidation states tend to have more ionic character and hence tend to have basic chemical character[29].

Thus, it would be interesting to compare the catalytic behavior of these three elements under a set of conditions of catalyst preparation and performance evaluation using model reactions. This aspect formed the main focus of this work.

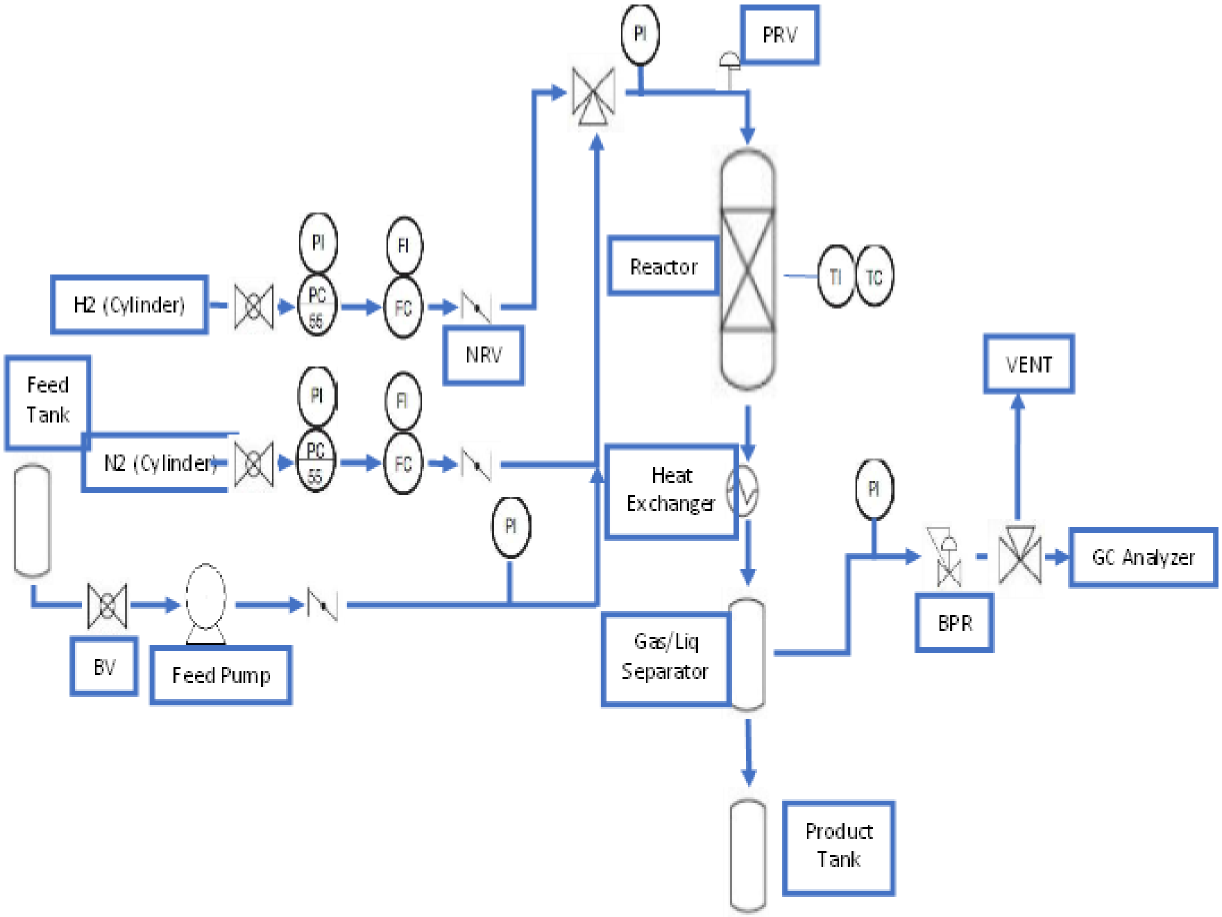
Most of the studies on conversion of styrene oxide reported in literature are carried out in batch reactors. Very few studies are reported in continuous flow mode. The current studies were carried out in a continuous flow reactor. Further, while Co, Ni and Cu based catalysts are reported for this reaction, the studies are fragmented. A systematic study comparing the behavior of these active metals under a given set of preparation and evaluation conditions is not reported in literature. Such a study will add value in understanding their behavior in light of the differences in their electronic properties. Most of the studies are with mono-component supports. Some studies with bi-component supports are reported, but a combination of zirconia-alumina is not reported in literature. Both alumina and zirconia are useful for acid catalysis. Thus supporting Co, Ni, Cu on bi-component zirconia-alumina supports would make an interesting study.

4.2 Experimental:

Schematic of the reactor set up used for the study is shown in Figure 4.1 below. The catalytic reaction studies were carried out in continuous flow ½” ID stainless steel reactor heated with a tubular furnace. H_2 was fed with Bronkhorst Mass Flow Controller. Pressure was controlled manually with a Tescom make back pressure regulator. Styrene oxide was fed using a Scientific Systems Inc. HPLC pump. The catalyst was tableted and sized to granules and the fraction between 0.5-0.8 mm was charged to the reactor. The catalyst bed was positioned in the isothermal zone of the furnace with glass beads at upstream and downstream. The catalyst was dried in nitrogen at 150°C (4h). The nickel and cobalt catalysts were reduced at 500°C whereas the copper based catalysts were reduced at 400°C. Basis was reduction profiles of TPR (Figure 3.14, chapter 3). The reactor was cooled to reaction temperature 150°C in hydrogen and pressurized to 10 bar g. Styrene oxide was fed along with hydrogen (H_2:Styrene oxide 2.75:1 molar). It was ascertained that this ratio was adequate. WHSV based on styrene oxide was 6 h^{-1}. Run length was 6 h on stream with hourly sampling of product.

The product was condensed in a double pipe heat exchanger and collected in a gas-liquid separator. It was analyzed with an Agilent 7890B Gas chromatograph with a 30m x 0.5 mm Innowax HP capillary column using FID detector and Helium as carrier gas. Retention times and response factors of the components of the feed and product were determined using calibration mixtures.

A brief schematic of the reactor unit is shown below:

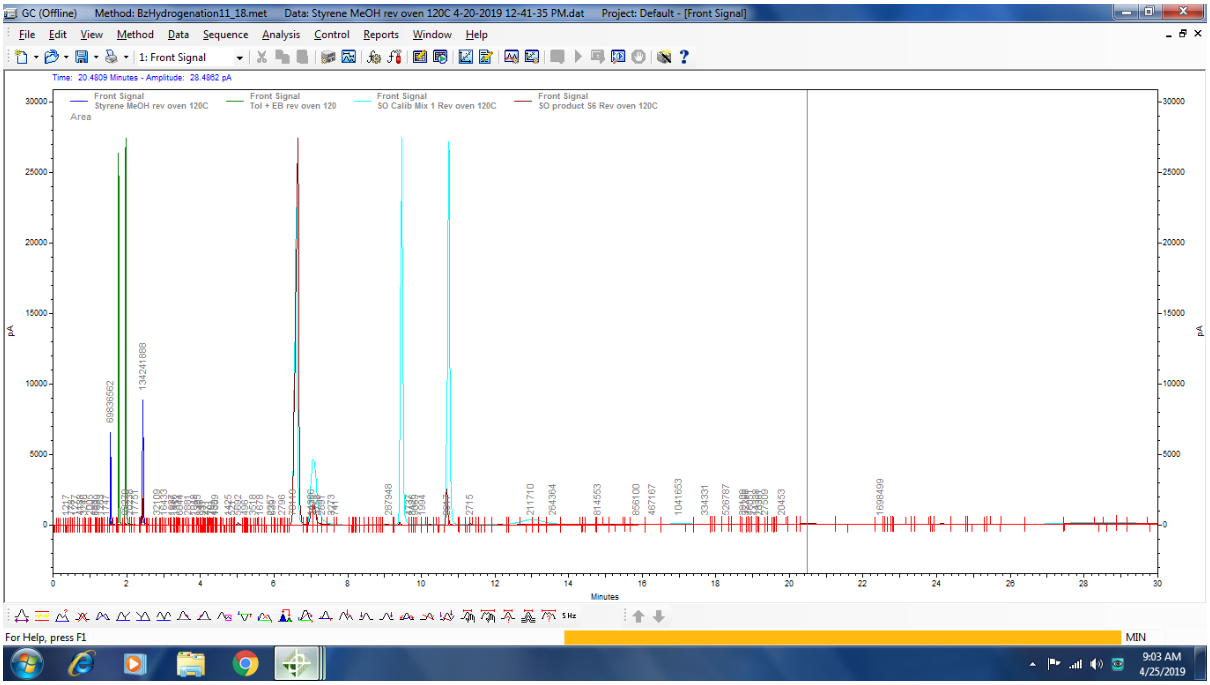


Legend: BPR = Back Pressure Regulator; BV = Ball valve; NRV = Non-return valve; PI = Pressure Indicator; PC = Pressure Regulator; PRV = Pressure relief Valve; FI = Flow Indicator; FC = Flow Controller; TI = Temperature indicator; TC = Temperature Controller

Figure 4. 1: Schematic of testing of catalysts for transformation of styrene oxide

Styrene oxide is a hazardous chemical. It is classified category 4 for flammability and dermal toxicity, category 3 for acute inhalation toxicity, category 2 for skin and eye irritation, category 1 for skin sensitization and category 1B for mutagenicity and carcinogenity. Hence, the entire reactor was housed in a ventilated walk-in enclosure. Personal Protective Equipment's such as safety goggles, breathing filter and nitrile rubber gloves were used while handling and sampling reactants and products. The product was stored in a separate toxic waste container and sent for toxic waste disposal to an authorized vendor. MSDS of the reactant and major products is given in Appendix 20.

A sample chromatogram of the calibration mixture used to identify the components is shown in Figure 4.2 below and also in Appendix-14. The retention times are presented in Table 4.1 below


GC (Offline)   Method: BzHydrogenation11_18.met   Data: Styrene MeOH rev oven 120C 4-20-2019 12-41-35 PM.dat   Project: Default - [Front Signal]

Time: 20.4809 Minutes - Amplitude: 28.4862 pA

Figure 4. 2: Retention time of various products/biproducts

Peak #	Component	GC retention time (min)
1	Toluene	1.77
2	EB	1.96
3	Styrene	2.41
4	Styrene Oxide (SO)	6.47
5	Phenylacetaldehyde (PAA)	7.01
6	1-Phenylethanol (1-PEA)	9.37
7	2-Phenyl ethanol (2-PEA)	10.67
8	Heavy ends	14.55 - 29.76

Table 4. 1: Components of products of styrene oxide reaction along with retention time

% Conversion of Styrene oxide was calculated as

$$\text{Conversion } \% = \frac{\text{Concentration of SO in reactant} - \text{SO concentration in product}}{\text{Concentration of SO in reactant}} \times 100 \quad \text{Equation 9}$$

Selectivity was calculated in two ways.

The product selectivity based on moles of styrene oxide reacted was calculated by the following equation

$$S_{i/SO} = \frac{\text{Mol component } i \text{ produced}}{\text{Mol SO converted}} \quad \text{Equation 10}$$

Relative selectivity between two products formed was calculated as

$$S_{i/j} = \frac{\text{Mol component } i \text{ produced}}{\text{Mol component } j \text{ produced}} \quad \text{Equation 11}$$

Where i and j are two products formed from two different reactions within the reaction network.

The latter method of calculating selectivity is very useful when there is a network of reactions such as in scheme 1 (Figure 4.3 below). It provides means of comparing between parallel reactions.

4.3 Results and Discussion

Unreacted styrene oxide (SO), phenylacetaldehyde (PPA), 2-phenyl ethanol (2-PEA), 1-phenyl ethanol (1-PEA) and styrene were the major products. Small quantities of ethylbenzene (EB), toluene and heavies were also identified in the product. Out of these phenylacetaldehyde and 2-phenyl ethanol are valuable products.

The above mentioned products are expected to form from generic reactions shown in Figure 4.3 below.

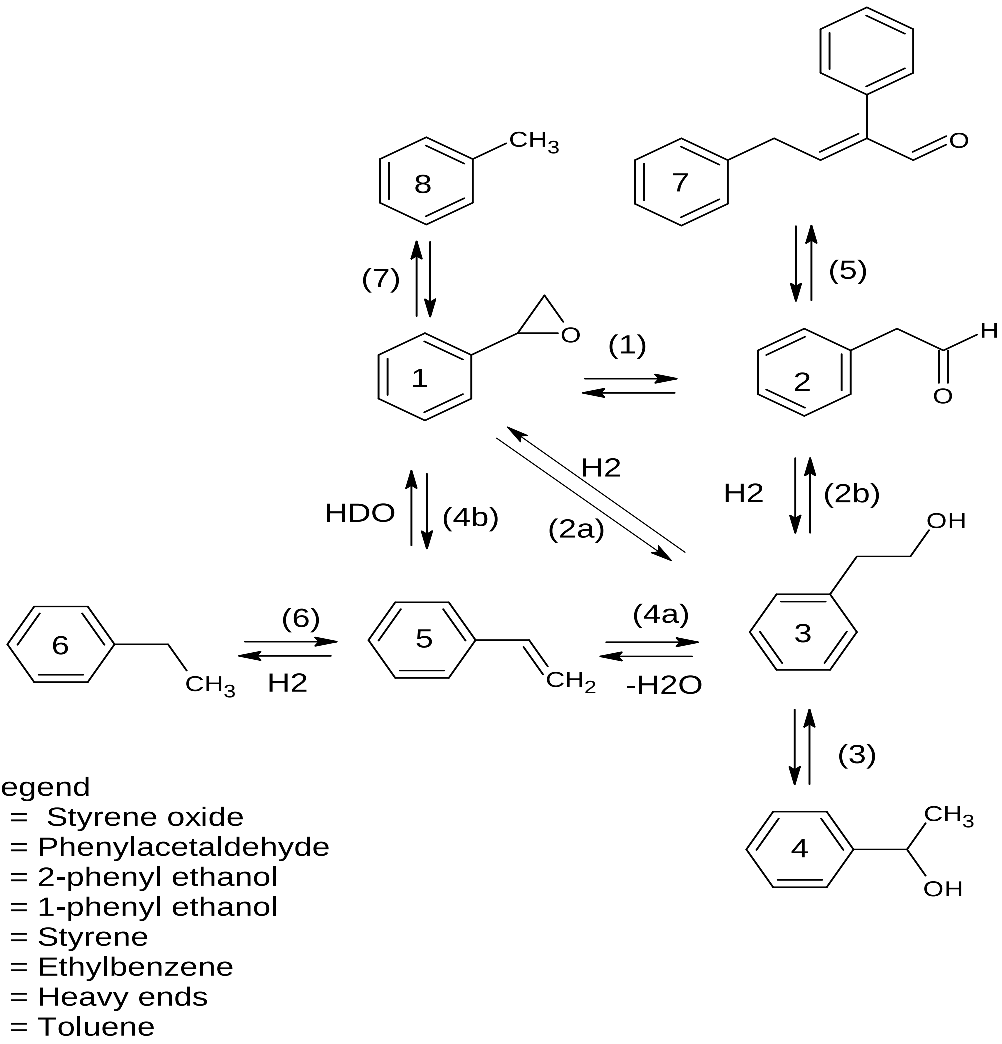


Figure 4. 3: Reaction scheme for transformation of styrene oxide

With reference of Figure 4.3, Styrene oxide isomerizes to PAA on oxide catalysts which do not contain reducible active metals such as Ni, Co, Cu, Pd or Pt[3][12][22][23][24][30][31][32][33][34]. Kirm et.al[9] also attribute isomerization of 2-PEA to 1-PEA to the oxide carriers used in their study. Thus, these isomerization reactions are catalyzed by acid function. Hydrogenation of styrene oxide to 2-PEA [9][12][13][14][15][16][22][23][24][24] on the other hand requires reducible active metals. Thus, it is catalyzed by metal function.

4.3.1 Trends of catalyst activity (Conversion)

Trends of conversion with time on stream are shown in Figure 4.4 a, b, c for the Cobalt, Nickel and Copper based catalysts.

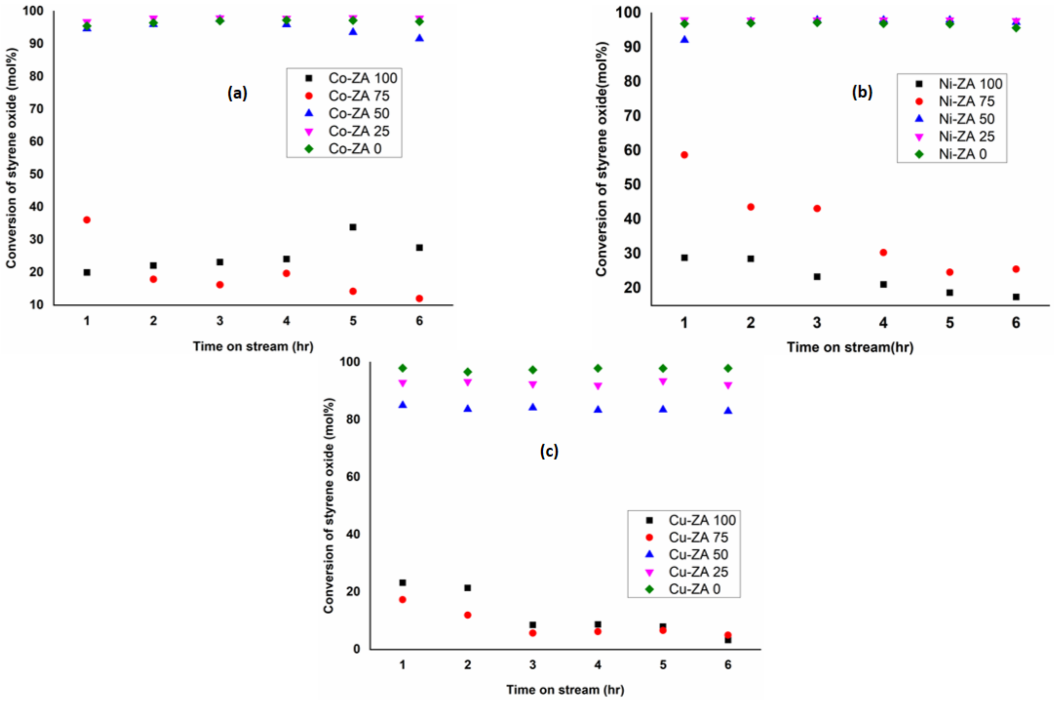


Figure 4. 4: Conversion of styrene oxide on a) Co-catalysts b) Ni-catalysts c) Cu-catalysts supported on zirconia-alumina

As seen from Figure 4.4 a, b, c there is a clear trend between conversion of styrene oxide and zirconia:alumina molar ratio of the catalysts. All the catalysts containing >25 mol% Al_2O_3 show conversion close to 96-99% while catalysts containing <50 mol% Al_2O_3 show conversion as low as 10%. Results of XRD (Figure 3.11, chapter 3) show that as alumina content in the catalysts increases, the crystallite size of the active metals (Ni and Co) decreases, which amounts to better dispersion of active metals resulting in more accessible active centres. However, it is worth noting that Cu based catalysts are an exception. Crystallite size of Cu increases as mol% of Al_2O_3 increases. This is because Cu shows stronger metal support interaction with ZrO_2 in contrast to the other two active metals (as seen from results of H_2-TPR, Figure 3.14, Chapter 3). Ni and Co show strong metal support interaction (MSI) with Al_2O_3 which minimizes sintering of these active metals during calcination thereby ensuring good dispersion on the surface. This results in higher conversion in catalysts. Samples with lower alumina and higher zirconia content i.e. samples with $ZrO_2 > 50$ mol% in the zirconia-alumina carrier composition show poor initial conversion accompanied by some deactivation irrespective of active metal. This behavior is attributed to the absence of active metals on the surface when they are supported on neat zirconia carrier (Chapter 3 XPS Figure 3.16 a,b,c). This affects both the reductive cleavage of styrene oxide and hydrogenation of PAA to 2-PEA. Surface concentration of active metals improves with decreasing zirconia content (Chapter 3 Figure 3.17 d, e, f XPS results). All three active metals are clearly observed on the surface on the M-ZA 0 catalysts (Figure 3.17 a, b, c) while they are absent in ZA 100 based composition. M-ZA 50 show weak active metals peaks. The results of XPS are also compiled in Figure 4.7 below for ready reference. Zirconia also affects acidity of the catalysts which in turn affects conversion of SO to PAA, thus contributing to low overall conversion. Copper catalysts tend to show relatively lower conversion for the same support composition. This indicates different behavior of Cu than Co and Ni. Surface concentration of Cu is less than that of Co or Ni based catalysts.

Hence, increase in mole% of zirconia in the system decreases the conversion of styrene oxide due to absence of active metals on the surface as well as low acidity.

4.3.2 Trends of Space Time Yield (STY) of 2-PEA, PAA and PAA+2-PEA

Space time yields are convenient for comparing across different studies / catalysts wherein catalyst activity / conversion could be different.

PAA is formed by isomerization of styrene oxide (reaction 1 in reaction scheme Figure 4.3), which is catalyzed by acid function of catalysts. 2-PEA is formed by hydrogenation of SO (reaction 2a in scheme) or of PAA (reaction 2b in scheme). Hydrogenation requires a metal function. Both PAA and 2-PEA are valuable products. A comparison of space time yields of PAA, 2-PEA provides insight into the extent to which the acid and metal functions vary with change in composition (zirconia and metal content) of the catalyst.

Space time yield was calculated from the space velocity of styrene oxide feed, its conversion and selectivity to a given product at steady state conversion as:

$$\boldsymbol{(STY)i} = \left(\frac{\boldsymbol{F}}{\boldsymbol{W}}\right)\textbf{SO} \times \textbf{fractional conversion of SO} \times \textbf{fractional selectivity of product 'i'}$$

Where $(F/W)_{SO}$ is space velocity of styrene oxide feed to the reactor.

A comparison of STY of PAA, 2-PEA and combined STY of PAA+2-PEA of the catalysts is provided in Figure 4.5 below.

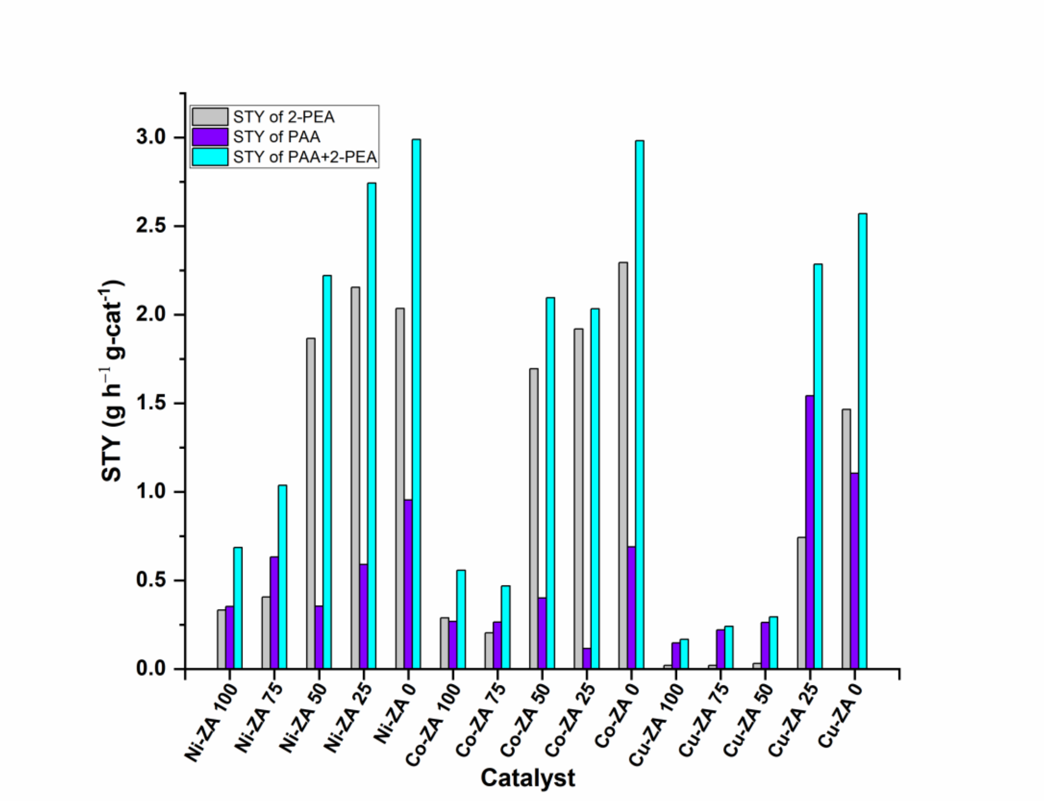
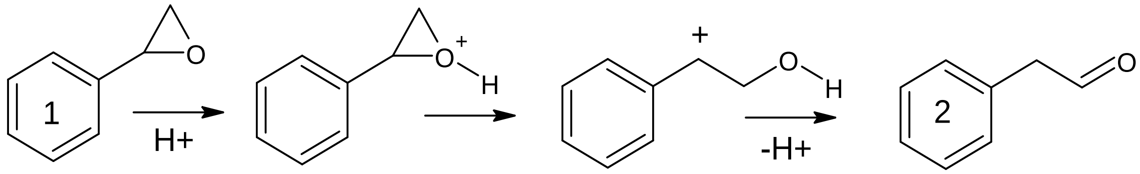


Figure 4. 5: Space Time Yields of 2-PEA, PAA and (PAA+2-PEA) on Co, Ni and Cu catalysts supported on zirconia-alumina

All the catalysts show increasing trend of STY with increasing content of alumina in the support. The trend is irrespective of the active metals. At high Zirconia content ≥75 mol%, STY of both PAA and 2-PEA are low in all the catalysts. Low STY of PAA is attributed to low acidity of the catalysts as described in TPD (Figure 3.13, chapter 3) when zirconia content of the catalyst is high. As explained earlier PAA forms by isomerisation of SO. Isomerisation function needs acidic sites. It follows a carbenium-ion mechanism as shown below[3]: 1 = SO; 2 = PAA



NH_3 TPD of supports (Figure 3.13, chapter 3) indicate the development of Lewis acidity as Al_2O_3 mol% in the support increases. This trend remained unchanged when active metals are loaded on the supports. The correlation of acidity with STY of PAA is shown in Figure 4.6 below.

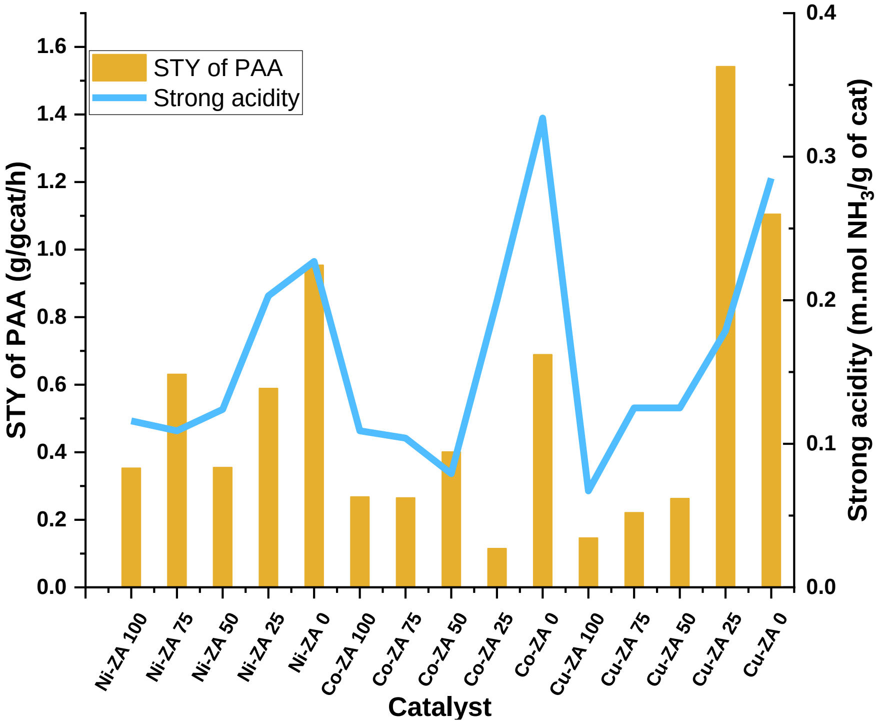


Figure 4. 6: Trends of STY of PAA and strong acidity by NH_3 TPD

Above figure correlates acidity of the catalysts with STY of PAA. As seen from figure 4.6 there is a strong correlation between strong acidity and STY of PAA. This is consistent with studied reported in literature which show that PAA is catalyzed by acid sites of the catalyst[3][12][13][22][23][24][30][31][33][34]. Trend for STY of PAA is Cu-ZA 25>Cu-ZA 0> Ni-ZA 0 > Co-ZA 0. Thus amongst the catalysts copper catalysts show better selectivity followed by Ni and then Co for formation of PAA. Catalysts supported on neat gamma-alumina or alumina rich supports gave highest yields, which is consistent with acidity trends of the catalysts in Figure 4.6.

STY of 2-PEA is presented in Figure 4.5. STY of 2-PEA is low for the catalysts with high zirconia content. It is well known from the reaction schematic (Figure 4.3) that 2-PEA is formed by hydrogenation of SO or hydrogenation of PAA. Transition metals i.e. Co, Ni and Cu present in the catalysts are capable of imparting hydrogenation function to the catalysts and catalyzing the reaction [8][9][10][11][12][13][14][15][16][17][18][19]. Although input concentration of the active metals (Co, Ni and Cu) is kept identical for all the supports, variation is seen in the STY of 2-PEA. STY of 2-PEA increases with decrease in ZrO_2 mol% in the supports. Supports with higher ZrO_2 content have lower metal dispersion due to lower specific surface area of the catalyst. This is supported by the higher XRD crystallite size (Figure 3.11, chapter 3). Cu based catalysts are exception to this. Poor metal dispersion results in less active centres. Apart from this, as seen from results of XPS in Figure 4.7 the concentration of active metals on the surface of the catalyst show a clear trend with zirconia content of the support. As evidenced from XPS surface concentration of active metals is inversely related to zirconia content of the catalyst.

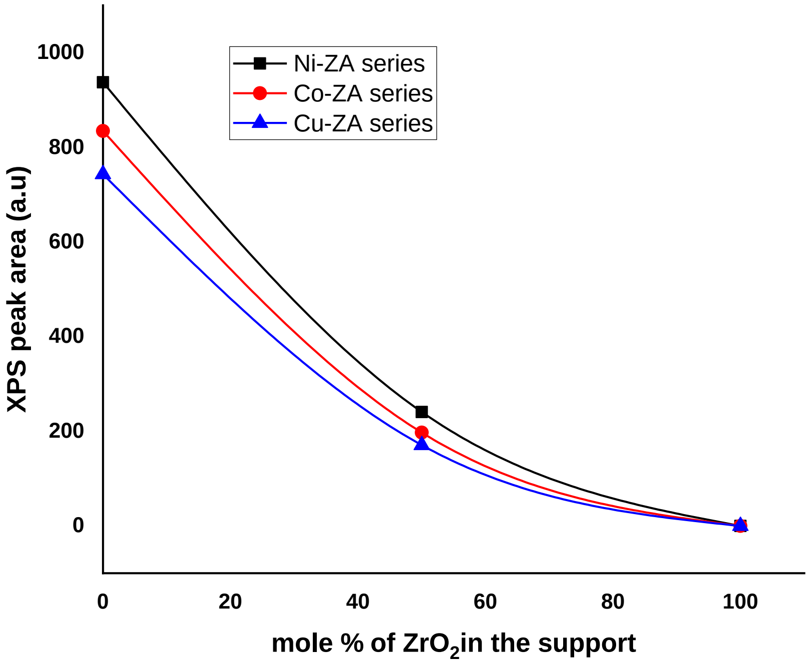


Figure 4. 7: Trend of surface concentration of active metals as a function of zirconia content of catalyst.

The low surface concentration of active metals in catalysts with higher zirconia content adversely affects both the reductive cleavage of styrene oxide and hydrogenation of PAA (which are responsible for formation of 2-PEA). Thus STY of 2-PEA is low on catalysts with high zirconia content and it increases as zirconia content of the catalyst decreases. The trend of STY of 2-PEA is Co-ZA 0 > Ni-ZA 25> Ni-ZA 0 > Co-ZA 25. Co and Ni catalysts with <75 mole % zirconia give significantly better yields of 2-PEA than the zirconia rich catalysts. The difference between them is small. The Cu catalysts show significantly less STY to 2-PEA than their Co and Ni counterparts. Thus Cu has inherently poor hydrogenation function when compared to Co and Ni catalysts.

Further, as seen from Figure 4.5 above the STY of PAA and 2-PEA are closer to each other for Ni and Co catalysts with high zirconia content (≥75 mole%). Whereas, in case of Cu catalysts STY of PAA is significantly higher than that of 2-PEA. This is irrespective of zirconia content. It is highly aggravated in catalysts with high zirconia content (≥50 mole%) where 2-PEA is practically absent. The reason for this appears to be preferential orientation (suppression) of Cu(111) plane in reduced catalysts. The ratio of intensity of the Cu(200)/Cu(111) plane is significantly higher in reduced Cu-ZA-100 and Cu-ZA 75 catalysts with high zirconia content (refer Figure 4.8 below). This indicates a decrease in intensity of Cu(111) plane. Ratio reported for Cu metal in XRD PDF4 reference is also included in the plot for comparison.

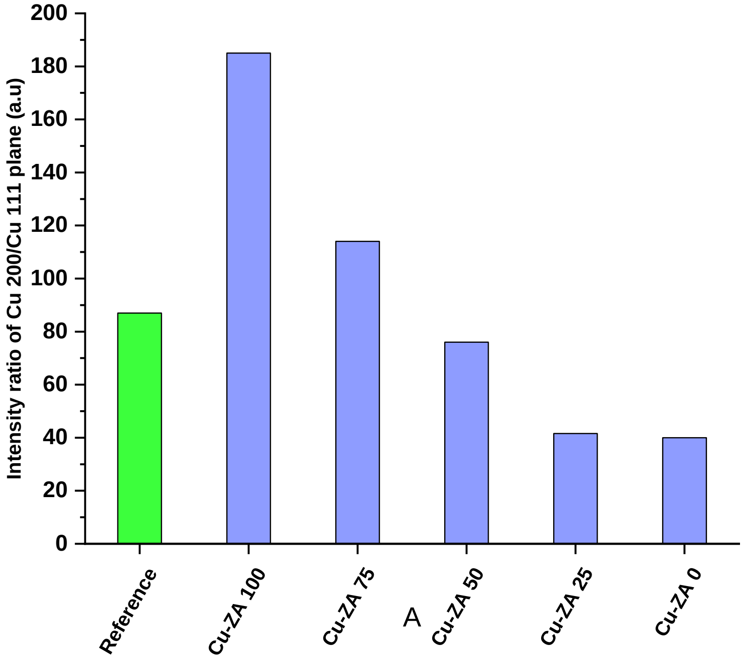


Figure 4. 8: XRD peak intensity ratio of Cu(200) and Cu(111) peaks of reduced Cu-ZA # series of catalysts

It is confirmed from XRD patterns shown in appendix 9 that the increase in this ratio is indeed due to a decrease in the intensity of Cu(111) peak with increasing zirconia content of catalyst. Thus, the trend of 2-PEA correlates with intensity of Cu(111). From this it is inferred that Cu(111) is responsible for the reductive cleavage of SO to 2-PEA (reaction 2a in Figure 4.3 above).Yu Jen Shih et.al.[35] have reported similar behaviour of Cu(111) for the reduction of NOx to N_2. They report that the rate constant for formation of reduction of NOx increases by 20% when the Cu(200)/Cu(111) intensity ratio decreases from 60% to 30% (effectively increase in Cu(111)).

As zirconia content decreases ≤ 50 mol%, acidity increases (Figure 4.6 above) because of which acid function of the catalysts improves and STY of PAA also increases in turn for all catalysts. Metal concentration on the surface of the catalyst also increases simultaneously (Figure

4.7 above) hence metal function also improves, resulting in an increase in STY of 2-PEA. STY of 2-PEA exceeds that of PAA because the latter is now converted to 2-PEA. However, in Cu catalysts the increase in 2-PEA is significantly lower than in the case of Ni or Co catalysts. The difference in behavior of Cu catalysts may also be attributed to the difference in its electronic configuration from that of Co or Ni as mentioned in the introduction section. It is also noted that Cu has a smaller ionic radius than Co and Ni because of which it has a relatively stronger acidic character.

Thus, the Cu based catalysts on zirconia rich carrier have a poor hydrogenation function compared to the Co or Ni based catalysts. Psaro and Ravasio[12] have shown in batch reaction studies of hydrogenation of styrene oxide in dioxane solvent that increasing zirconia (from Zr:Si 1 to 4.7) in SiZr supports, favors the formation of PAA (selectivity increases from 2% to 66%) relative to 2-PEA (which decreases from 80% to 14%) on 8% Cu/SiZr catalyst. Thus, higher zirconia favors formation of PAA relative to 2-PEA at the same active metal content.

Their results also show that decreasing Cu content from 8% to 5% on silica doped with 1 wt% zirconia lowers selectivity of 2-PEA from 80% to 8% with concomitant increase in selectivity of PAA from 2% to 33%. Thus, hydrogenation function is strongly dependent on availability of Cu. The results of the present study also show that Cu/zirconia-alumina supports with high zirconia content favor the formation of PAA due to poor availability of Cu on the surface of the catalyst. Hence, the combination of Cu and zirconia appears to have a similar effect in both silica and alumina carriers. The results of the current study are in agreement with those of Ravasio et al.[12] in this respect.

4.3.3 Trends of side reactions (Relative selectivity between formation of styrene and formation of 2-PEA):

Apart from 2-PEA and PAA other byproducts also formed in the reaction as seen from table 4.1

Styrene can form by deoxygenation of SO as well as by dehydration of 2-PEA (reactions 4a or 4b in scheme 1 Figure 4.3 respectively). The deoxygenation of styrene oxide (4a) which forms styrene is a competing reaction to the formation of 2-PEA from styrene oxide.

Formation of styrene and ethylbenzene has been reported by Hoelderich et.al[11] over copper loaded on zeolitic supports and by Kirm et.al.[10] with 2 wt% Pt supported on carriers such as γ-alumina, MgO and activated carbon. Psaro et.al.[12] also report their formation in batch reactor studies over copper supported on silica, silica-alumina and silica-zirconia.

Formation of styrene is attributed to deoxygenation of styrene oxide on various catalysts: by Sasu et.al.(nickel hydrotalcites)[13], Miyano et.al. (metal halides with Zn-Cu couple),[36] and Kinjenski et.al. (thermally dehydrated MgO),[37]. Sooknoi and Dwyer[38], Lange and Otten[39] attribute formation of styrene to dehydration of 2-PEA over acid sites on metal free oxide catalysts and zeolites. Jixiang Chen et.al[40] report that spill-over hydrogen at interface of intermetallic Ni_3Ga and SiO_2 support leads to hydrodeoxygenation of anisole to benzene.

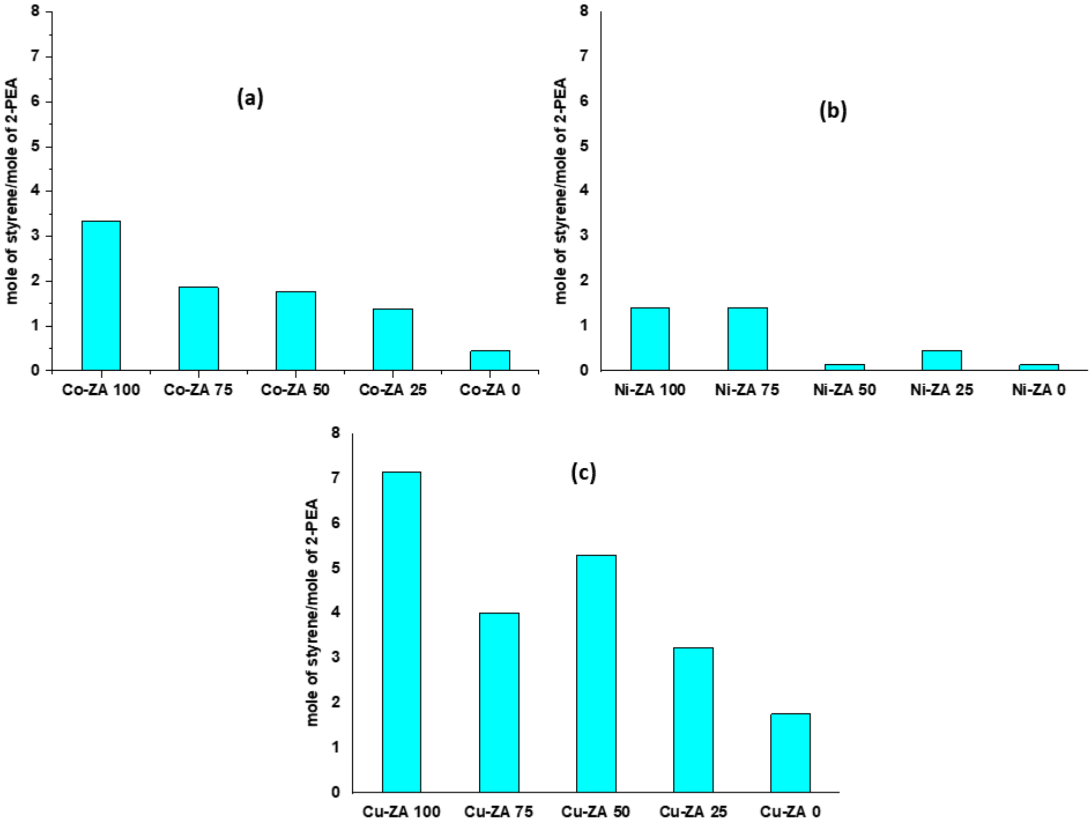


Figure 4. 9: Relative selectivity between formation of styrene and 2-PEA on a) Co-catalysts b) Ni-catalysts c) Cu-catalysts supported on zirconia-alumina

The formation of styrene by deoxygenation is a competing reaction to the formation of 2-PEA (by reductive cleavage of SO) and also to formation of PAA (by isomerization of SO). The relative selectivity of styrene to 2-PEA is calculated for the Co, Ni and Cu catalysts and shown in Figures 4.9a, b and c. As seen from these Figures the propensity for the formation of styrene increases with the concentrations of zirconia in the catalyst. This is irrespective of the metal Ni, or Co or Cu. However, the copper based catalysts (Figure 4.9c) show 2 to 5-fold higher relative selectivity to styrene than their cobalt and nickel counterparts respectively. Trend for relative selectivity of Styrene:2-PEA is Cu >> Co > Ni catalysts.

It is noted that the formation of PAA is an acid catalyzed reaction whereas the formation of 2-PEA and styrene oxide (by hydrodeoxygenation) are metal catalyzed reactions. Ammonia TPD shows that acidity is low in catalysts which are rich is zirconia. This should retard the formation of PAA and favor the metal catalyzed reactions (formation of styrene and 2-PEA) in these catalysts. While formation of styrene is indeed favored, it is observed that the ratio of styrene:2-PEA is significantly different in these three sets of catalysts. This trend in selectivity to styrene correlates with trend of preferential orientation of XRD crystal planes (111 plane of CuO) in Cu catalysts and (200 plane of Co_3O_4) in Co catalysts with high zirconia content (Table 3.8 XRD results Chapter 3). The reduced catalysts also show the same trend for intensity of Cu (111) plane in Cu-ZA series (see ratio of Cu(200)/Cu(111) in Figure 4.8 above). Thus, the suppression of the Cu(111) plane favors formation to styrene at the expense of 2-PEA (which is a competing reaction). Yu Jen Shih et.al[35] have reported similar correlation of Cu(111) for the reduction of NOx to N_2. Effect of preferential orientation of Cu(200)/graphene[41] (for oxidation, reduction and coupling reactions) and of Au(111)/CeO_2[42] (for CO oxidation) is reported. Thus the referred orientation of crystal planes of Cu and Co appear to influence the selectivity to styrene.

The strikingly different behavior of the copper catalysts may also be attributed to differences in electronic properties of these three active elements. The Fermi level not overlapping with the d band of Cu. It is 0.1 eV lower than the d band. Whereas, the d bands of both Ni and Co overlap with the Fermi level[28]. Quaino et.al.[28] have shown from model Hamiltonian, quantum statistics and DFT calculations, that, an overlap of the d band and the Fermi level is one of three important criteria for good catalytic activity in hydrogen electrocatalysis.

Another contributor could be the difference in electronic properties of copper when compared to Ni or Co. Co, Ni and Cu are from the first transition series of the periodic table. The electronic configuration of Cu ($4s^1 3d^{10}$) shows anomalous behavior from that of Co ($4s^2 3d^7$) and Ni ($4s^2 3d^8$) in that, the 3d orbital is completely filled before the 4s orbital, which is half filled. The Allen scale electronegativity increases from Sc (1.19) to Co (1.84) and Ni (1.88) and then decreases for Cu (1.85) and Zn (1.59). The Pauling scale also shows a similar trend. Cu tends to have I and II (lower) oxidation states, where as Co tends to have II, III, IV, V and Ni II, III, IV (higher) oxidation states. Oxides of lower oxidation states tend to have more ionic character and hence tend to have basic chemical character[43]. Whereas, decreasing ionic radius along a period increases electronegativity because of which acid character increases. Thus, the acidity is a combined effect of these parameters.

Another route of formation of styrene is dehydration of SO. Dehydration reaction requires acidity. The catalysts (having >50 mol% ZrO_2) which show higher selectivity to styrene have low strong and total acidity (Figures 4.6 above and Figure 3.13 Chapter 3), hence the formation of styrene by dehydration (reaction 4a in Figure 4.3) is deemed unlikely. Strong hydrogen spill-over effect (Figure 3.15, chapter 3) is also associated with higher zirconia content. The liquid reaction product in these cases showed hazy appearance due to finely dispersed droplets of water which is a product of hydrodeoxygenation. Thus our results are aligned with the formation of styrene by the hydrodeoxygenation of SO which is enhanced by spillover hydrogen.

4.3.4 Minor by-products

Small quantities of ethylbenzene (EB) and toluene were also detected in the products. EB is expected to form by the hydrogenation of styrene. Trace amount of toluene was also observed in the products of all the samples. Formation of EB and toluene is also reported by Hoelderich et.al.[11] Toluene is reported to form by hydrogenolysis of ethylbenzene[44].

Kochkar et.al.[30] report deactivation due to aldolization on basic catalysts resulting in the formation of 1,3,5-triphenylbenzene which leads to fouling. Deactivation by trimerization of PAA is reported on strongly acidic catalysts (zeolites)[23]

Trend of selectivity for heavy product which could not be characterized was (Ni catalysts (2-8 mol%) < Co catalysts (7-16 mol%) < Cu catalysts (7-22 mol%). It may be responsible for deactivation of the catalyst with higher zirconia content. Considering the low acidity of these catalysts, their deactivation is attributed to aldolization reactions.

4.3.5 Trends of isomerization of 2-PEA to 1-PEA

2-PEA is the desired isomer. Trends of positional isomer selectivity of 2-PEA:1-PEA are shown in Figures 4.10 a, b, and c for the cobalt, nickel and copper based catalysts.

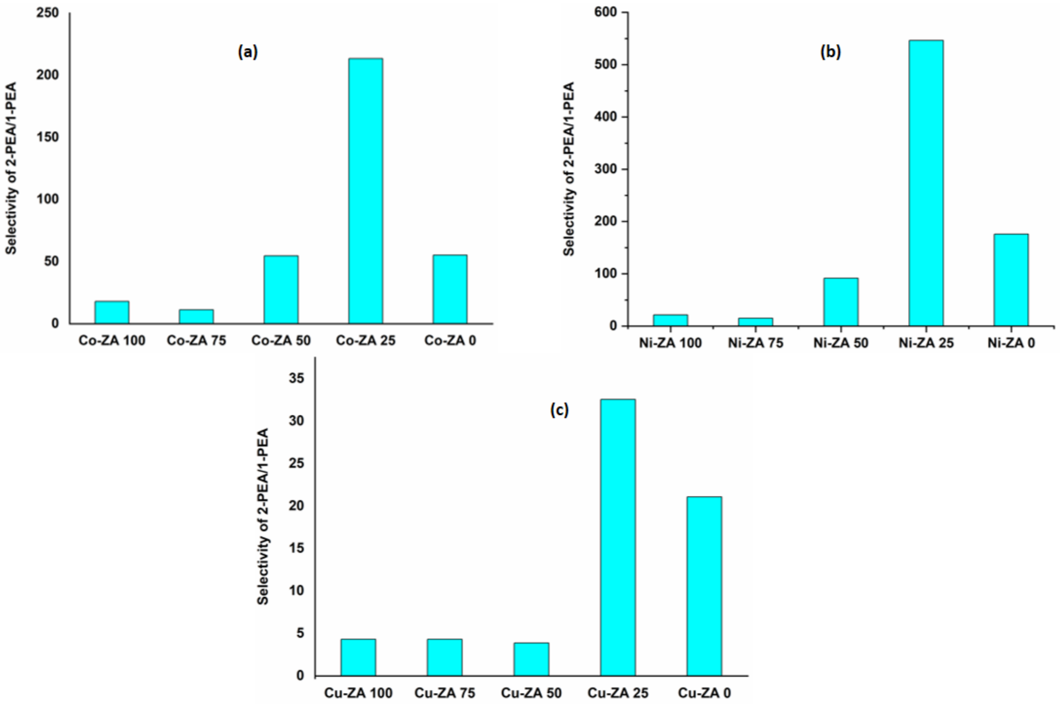


Figure 4. 10: Positional isomer selectivity of PEA on a) Co-catalysts b)Ni-catalysts c) Cu-catalysts supported on zirconia-alumina

Kirm et.al.[10] have reported formation of 1-PEA in addition to 2-PEA over 2 wt% Pt supported on γ-Al_2O_3, activated carbon and MgO carriers, whereas they report that it was not detected in the case of 2 wt% Pd on MgO[9]. In the current study formation of small quantities of 1-PEA (undesired isomer) was observed in all the samples. Samples with higher alumina content showed significantly lower selectivity to 1-PEA. Alumina is amphoteric in character. As seen from Figures 4.10 a, b and c catalysts prepared with carrier containing 25 mol% zirconia give significantly higher selectivity to desired isomer (2-PEA) within a given active metal series. Between the metals the trend of isomer selectivity to 2-PEA is Ni-ZA 25 >> Co-ZA 25 >> Cu-ZA 25.

4.3.6 Effect of Process Parameters

As seen from Figure 4.3 (Reaction scheme). The isomerization of SO to PAA is a unimolecular reaction whereas its hydrogenation to 2-PEA is bimolecular with a decrease in moles. Further, formation of PAA and 2-PEA from SO are parallel reactions. 2-PEA also forms from hydrogenation of PAA. Styrene can form from the dehydration of 2-PEA or from HDO of SO. The effect of temperature, pressure, H_2/HC molar ratio and space velocity were studied over Ni-ZA 25 catalyst which gives amongst the best performance for 2-PEA, combined PAA+2-PEA space time yields and isomer selectivity to 2-PEA amongst the bicomponent zirconia-alumina catalysts. It has a bicomponent carrier with 25 mol% zirconia and 75 mol% Al_2O_3 with a nominal Ni content of 12 wt%.

4.3.7 Effect of reaction temperature

Time on stream trends of reaction temperature are shown in Figure 4.11 below. The reaction conditions were temperature (variable), WHSV 6.18h^{-1}, pressure 10 bar g, H_2/SO 5.2 (mole). It was ascertained upfront that H_2/SO >2.5 did not affect conversion of SO.

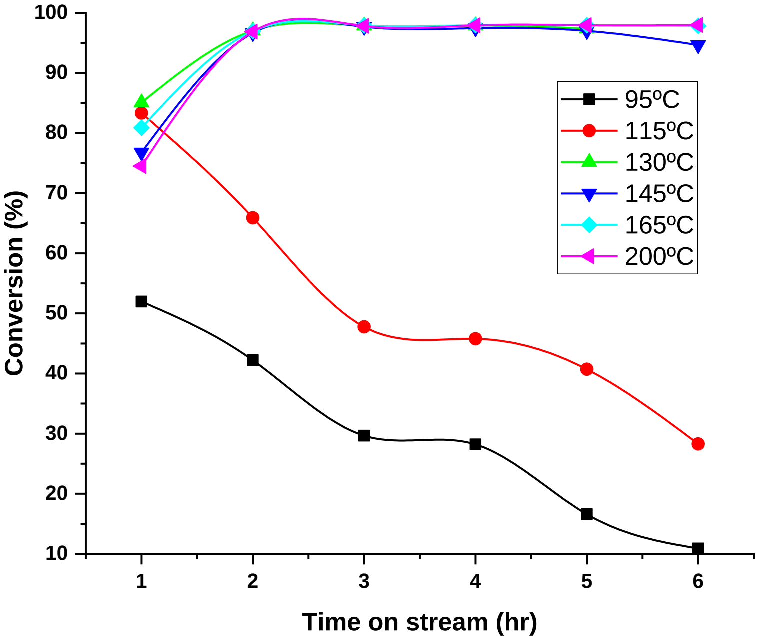


Figure 4. 11: Trend of time on stream conversion of styrene oxide as a function of reaction temperature.

As seen from Figure 4.11 above stable conversion is observed (about 97-98%) when reaction temperature is ≥130°C. However rapid deactivation is observed when temperature is <130°C. Trend of product selectivity is presented in Figure 4.12 below. As seen from the trend of product selectivity (Figure 4.12), formation of 2-PEA is significantly low at these latter temperatures. Thus, more PAA (which otherwise hydrogenates to 2-PEA) is available for the formation of heavy ends by aldol condensation. Stable conversion is observed at temperature ≥130°C where the hydrogenation activity is good and PAA hydrogenates to form 2-PEA. In view of these results all the catalysts were tested at 150 °C, 10 bar g, H2/SO 5.2 molar and WHSV 6.18 h^{-1}. Where a particular reaction parameter was varied, the remaining parameters were maintained at these cited values.

Lined out conversion and product selectivity as a function of reaction temperature is shown in Figure 4.12 below. Temperature was varied in the range 95 to 200°C.

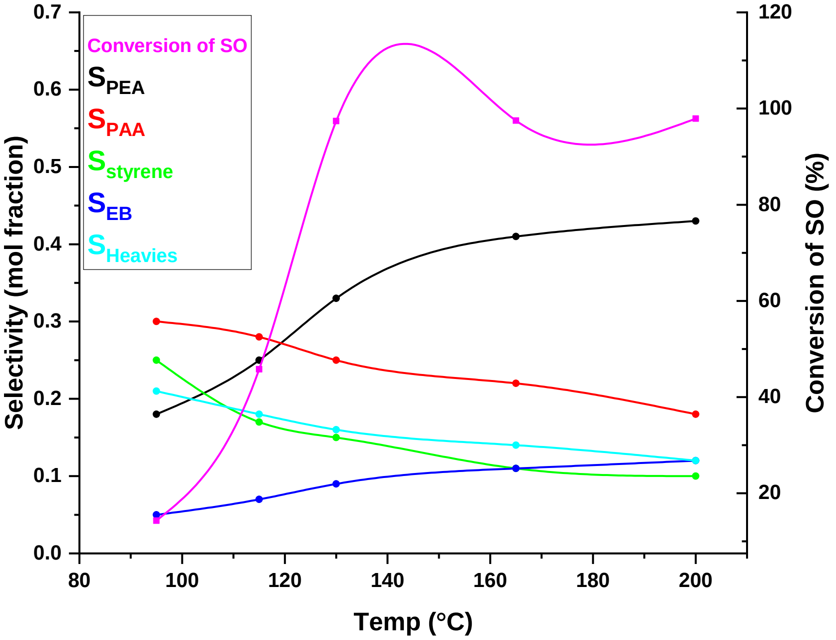


Figure 4. 12: Trends of steady state conversion of styrene oxide and selectivity to key products as a function of reaction temperature

As seen from Figure 4.12 above, conversion of SO, and the selectivity of 2-PEA and EB increase with temperature whereas that of PAA and styrene decreases. This is consistent with the reaction scheme wherein PAA and 2-PEA form from SO through parallel reactions, Further PAA gets hydrogenated to 2-PEA. Styrene formation by hydrodeoxygenation is also a competing reaction to formation of PAA and 2-PEA. EB forms by the hydrogenation of styrene. Thus temperature appears to favor the hydrogenation function over the acid function. Concentration of heavies is significant at lower temperatures. The rapid deactivation observed at lower temperatures (Figure 4.11) can be attributed to the formation of heavies which are products of aldol condensation.

4.3.8 Effect of reaction pressure

The isomerization of SO to PAA is a unimolecular reaction whereas its hydrogenation to 2-PEA is bimolecular with a decrease in moles. The hydrogenation of styrene to EB is similar to the latter reaction. The effect of pressure on conversion and product selectivity is shown in Figure 4.13 below.

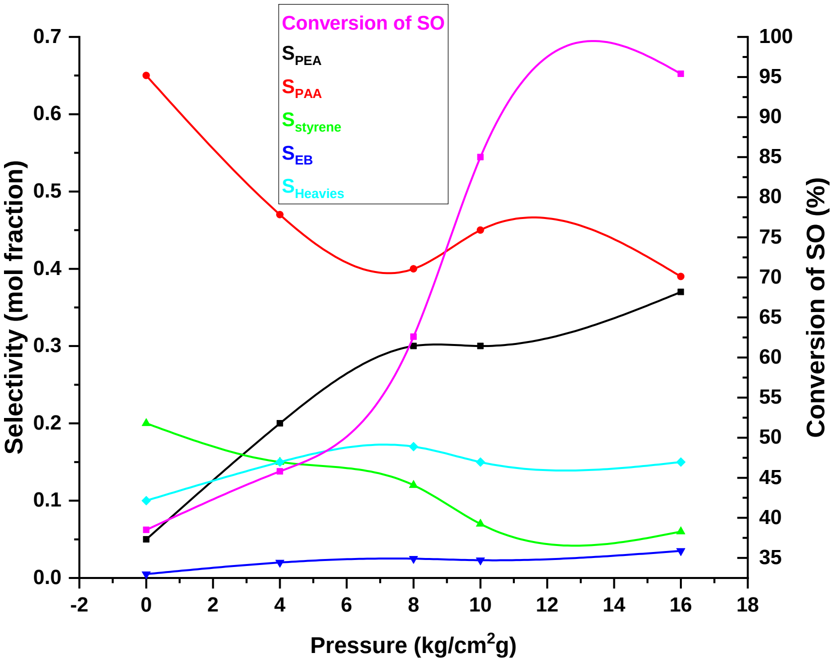


Figure 4. 13: Effect of reaction pressure on conversion of styrene oxide and selectivity to key products

As seen from Figure 4.13, increasing pressure clearly favors the bimolecular hydrogenation reactions where there is a decrease in moles. Both 2-PEA and EB show an increase at the expense of PAA and styrene. Heavies which are suspected to form by aldol condensation show an increasing trend with pressure up to 8 kg/cm^2 g. These trends are in line with expectation from the Le-Chatelier principle. Effect of pressure appears to flatten above 10 kg/cm^2 g.

4.3.9 Effect of space velocity

The effect of space velocity (WHSV) is shown in Figure 4.14 below

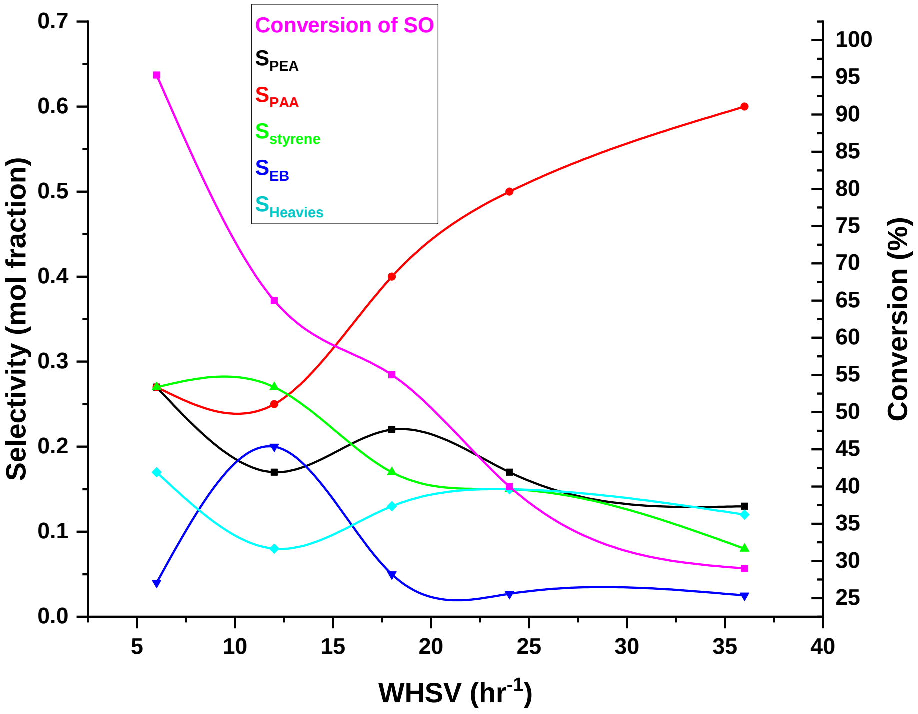


Figure 4. 14: Effect of space velocity on conversion and product selectivity

As seen from the above Figure, Conversion of SO decreases with increasing WHSV which is in line with expectation. Selectivity to PAA increases with WHSV. This is consistent with a sequential reaction scheme where SO isomerizes to PAA and the latter hydrogenates to 2-PEA. The hydrogenation reactions appear to be favored at lower WHSV. Heavies did not show a trend.

4.3.10 Catalyst regeneration studies

In order to check for regeneration, catalyst Ni-ZA 25 was regenerated twice. The regeneration procedure consisted of a wash with methanol at room temperature to remove organic reaction product from the catalyst. This was done keeping in mind health hazard of styrene oxide. The catalyst was then dried in air at 120°C for 4h and subjected to a temperature ramp 2°C/min up to 350°C at which temperature it was held for 2h. Then temperature was further ramped at 2°C/min to 500°C where it was held for 4h before cooling to ambient temperature. The regenerated catalysts were tested at 150°C, 6h^{-1}, 16 bar g and H2/SO 5.2 molar in a fixed bed continuous flow reactor. Results of conversion and selectivity to major products are shown in Figures 4.15 and 4.16 below.

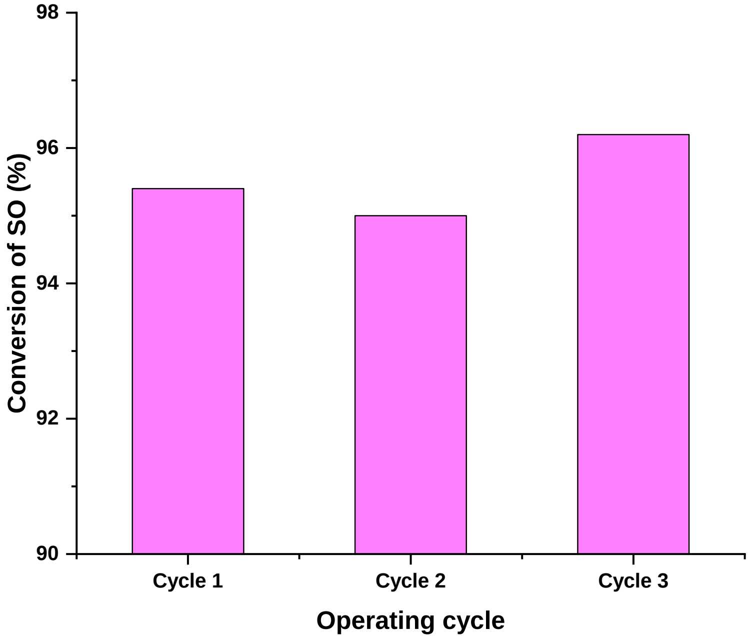


Figure 4. 15: Conversion of styrene oxide on regenerated Ni-ZA 25

As seen from Figure 4.15, the activity of the catalyst is reasonably constant over three cycles of regeneration.

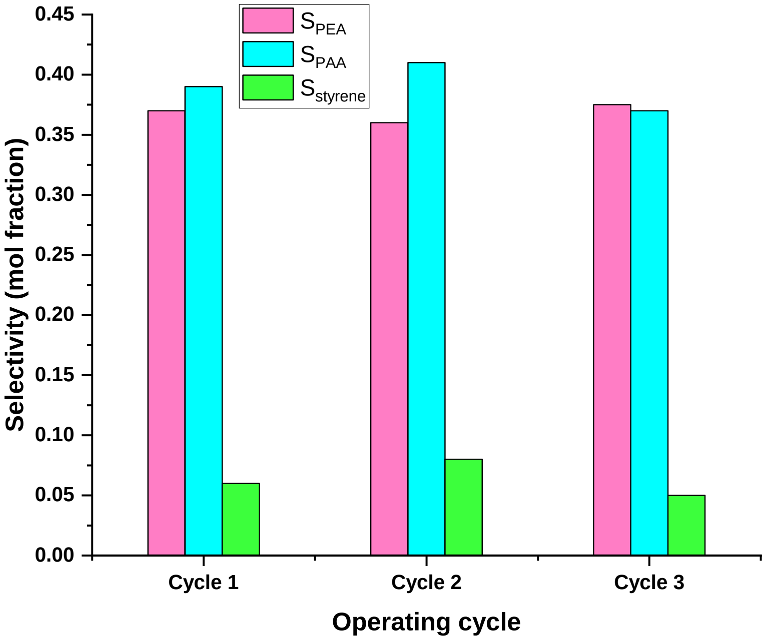


Figure 4. 16: Product selectivity on regenerated Ni-ZA 25

As seen from Figure 4.16 product selectivity is reasonable stable over three cycles of regeneration. Thus, the catalyst is deemed regenerable.

4.4 Conclusions

Co, Ni and Cu catalysts supported on bicomponent zirconia-alumina supports with varying ZrO_2:Al_2O_3 molar ratio were studied for the transformation of styrene oxide in continuous flow reactor studies. The supports were prepared by deposition precipitation. As seen from results presented in chapter 3 deposition-precipitation of zirconia on γ-Al_2O_3 significantly improves properties such as specific surface area and pore volume of the bi-component support relative to neat zirconia.

Also seen from results in Chapter 3, zirconia has a profound influence on many properties of the catalysts. Increasing zirconia content of the carrier decreases surface concentration of active metals as evidenced by XPS, decreases acidity and also decreases specific surface area. Whereas propensity for hydrogen spill increases. Preferred orientation of crystal planes is observed in Co and Cu catalysts which are rich in zirconia which affects selectivity to 2-PEA and styrene. Copper shows stronger metal support interaction (MSI) with zirconia whereas Ni and Co show strong MSI with alumina. MSI reflects in their crystallite size determined by XRD.

Raman spectra show trends with change in crystallite size in case of Ni catalysts and with preferred orientation of crystal planes in case of Cu catalysts.

Activity (expressed as conversion) for transformation of styrene oxide correlates well with surface concentrations of active metals as determined by XPS, acidity and also with crystallite size determined by XRD (presented in chapter 3).

The transformation of styrene oxide on these catalysts shows significant differences in activity and product selectivity between Cu on one hand and Ni and Co on the other. The Co based catalysts show the highest activity for formation of 2-PEA, closely followed by Ni based catalysts.

The Cu based catalysts show low activity for 2-PEA but high activity for PAA indicating relatively poor metal functionality.

Higher zirconia content decreases acidity which affects STY (Space Time Yield) of PAA. Surface concentrations of active metals are also low in this case, because of which hydrogenation activity is also retarded. Thus, STY of 2-PEA is also low. Hence, high zirconia content in catalyst affects formation of both PAA and 2-PEA. Cu based catalysts (especially in combination with high zirconia content) show poor hydrogenation activity as evidenced by the relative STY of PAA and 2-PEA.

Styrene is observed to form by the hydrodeoxygenation of styrene oxide. Spill over hydrogen and preferential orientation of crystal planes correlate with the formation of styrene. Copper catalysts show significantly higher selectivity for styrene than the Co or Ni catalysts. Cobalt catalysts also show a similar trend but to a smaller extent. The trend of selectivity to styrene correlates with preferential orientation of crystal planes of copper and cobalt catalysts

Differences in MSI (metal support interaction) between the active metal components and the zirconia or alumina components of the support are also observed. These reflect in the crystallite size determined by XRD and also in activity for conversion of styrene oxide.

Trends of conversion and product selectivity with changes in reactions conditions viz. temperature, pressure and space time are consistent with theoretical expectations of the reaction and the proposed mechanism of the reaction. Ni-ZA 25 could be regenerated twice.

Ni-ZA 25 is deemed the best catalyst based on STY to 2-PEA, PAA and isomer selectivity to 2-PEA.

Formation of styrene by-product needs to be suppressed significantly in non-noble metal based catalyst to improve yields of PAA and 2-PEA. The results show that increasing acidity of the catalysts helps in this respect. The results provide insights for further improvement of these catalysts.

4.5 References

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