Chapter-5 : HYDRODEOXYGENATION OF m-CRESOL

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 hydrodeoxygenation of m-cresol.

MSI (metal support interaction) and its effect on active metal sintering and redispersion of active metal precursors in calcined and reduced catalysts is studied.

Effect of zirconia content which affects characteristics of these catalysts such as acidity, their XRD crystallite size, surface concentration of active metals (XPS), MSI (metal support interactions) (as covered in chapter 3) is correlated with activity and product selectivity of these catalysts for hydrodeoxygenation of m-cresol.

Correlation of acidity and other properties with major class of reactions in hydrodeoxygenation, such as, DDO (Direct deoxygenation), HDO (Hydrodeoxygenation) and HYD (Hydrogenation) and TAU (Tautomerization) is attempted. Influence of acidity, metal functionality (XRD crystallite size, surface concentration by XPS) and oxophilicity on mechanism / product selectivity is examined.

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.

5.1 Introduction

The conversion of biomass to valuable chemicals is a sustainable alternative to fossil fuels for the manufacture of chemicals due to its renewable nature. Cellulose and hemicellulose components of biomass have been well studied and routes for their valorization are quite well established. Cellulose and hemicellulose are relatively easily converted to materials such as paper, value added compounds such as cellulose ethers and esters, levulenic acid, γ-valerolactone and 2G ethanol, through the exploitation of the sugars, HMF and furfural platforms [1].

Lignin is a component of biomass which has potential for valorization. The lignin component is however relatively difficult to valorize. It is a biopolymer of its monolignols coumaryl, coniferyl and sinapyl alcohols. It forms a range of phenolic compounds upon its thermal degradation. Lignin accounts for 5-35% of the weight of biomass depending on the type of vegetation. It is a low value by-product of the paper and pulp industry [2]. It is mainly used as fuel. Thus, efforts to valorize it to value added chemicals is important. Deoxygenation is a promising route for its valorization to chemicals such as BTX, cyclohexane, phenolics, xylenol, cyclohexanol, cyclohexanone and their methyl and dimethyl derivatives. These find use in the manufacture of polyester and nylon, fuels, aromatics, solvents, plastics, resins, adhesives, detergents and antioxidants.

Key reactions involved in valorization of compounds present in lignin are direct deoxygenation, hydrogenation, dealkylation and disproportionation which requires catalysts which are bifunctional[3][4]. Hydrodeoxygenation of phenol, phenol derivatives and biomass have been reported in literature. A variety of catalysts such as noble metal based catalysts: Pt/SiO_2[5], bimetallic Pt-Mo/Al_2O_3 [6], Pt/Al_2O_3 [7] and non-noble metal based catalysts such as supported metal oxide catalysts based on Co, Ni or Cu oxides[8][9][10][11] and metal sulfide catalysts such as MoS_2, CoMoS and NiMoS[12] on a variety of supports have been studied and reported for this reaction. Zhang et.al. have provided a comprehensive review covering these materials[13]. There is possibility to further explore non-noble metal catalysts for this reaction.

A number of studies have been carried out towards identifying heterogeneous catalysts for its hydrodeoxygenation and identifying the associated mechanism. Most of the studies are carried out with model compounds[14] such as phenol, cathecol, guaiacol, m-cresol, p-cresol or anisole which are representative of the complex phenolic components of lignin.

Noble metals like Pd[15] for phenol, Pt[16][17] for m-cresol, and Ru[18][17] for m-cresol are reported. Similarly, non-noble metals such as Ni and Co are widely studied as monometallic catalysts or bimetallic[10][16] Co-Mo for cresols, Ni-Mo[8] for m-cresol, Ni-P[19] for m-cresol, Pt-Mo[6], Ni-Cu[20] for anisole, bimetallic Ni with Co or Sn or Fe supported on SiO_2 for p-cresol[10]. Oxides such as MnO, WO_3, MoO_3, V_2O_5 supported on C are also screened by Mortensen in his doctoral thesis[21]. Oxophilic oxides such as MoO_3 and NbOx are studied in combination with Pt[22][6].

A variety of carriers silica[14][21], alumina[14][21], titania[14][21], ceria[14][21], ceria-zirconia[14][21], magnesium aluminate[21], zeolites USHY or HSZM-5[23], H-BEA or Ga-BEA[24][25], mesoporous silicas[11] carbon[21][14] have been reported in literature.

Based on the above literature, the noble and transition metals are reported to promote hydrogenation, direct deoxygenation, hydrodeoxygenation and hydrogenolysis whereas the oxide supports catalyze reactions such as dehydration, dealkylation, transalkylation, disproportionation and cracking[26]. Hydrogenation function, acidity and oxophilicity[6] are identified as important properties in these catalysts. Thus a combination of active metals with hydrogenation function and oxide materials (bi-functionality) is necessary for hydrodeoxygenation to form aromatics or cycloalkanes effectively[26].

Studies are reported in both continuous flow reactors as well as batch reactors. Temperatures range from 200 – 400°C, pressures atmospheric to 200 bar, W/F 0.1 to 70 g cat h/mol, H_2:organic substrate 12-400 molar. Some studies with phenol and m-cresol as substrate use solvents such as ethanol[27], water[21], cyclohexane[28]. Use of Solvents such as decane, decalin, dodecane, 1-octanol and hexadecane for batch hydrodeoxygenation of various (substituted)phenolics are reviewed by Paivi et.al.[14].

A number of mechanisms / reaction networks are proposed to explain the products formed[6][15][29][30]. These constitute combination of reactions such as Direct deoxygenation (DDO) or hydrogenolysis, Hydrodeoxygenation (HDO), Hydrogenation (HYD), Hydrodealkylation (HDA) and transalkylation. Based on these studied reported in literature the mechanism depends on the combination of active metal and oxide support as well as reaction conditions, which is compiled by Lei Nie[29]. Bifunctionality is important for the formation of BTX (aromatics Benzene-Toluene-Xylene) since the acid function has synergy with metal function. Metal function is required for hydrogenation and acid function for deoxygenation by dehydration[26]. Oxophilicity of promoters or supports is reported to influence formation of Toluene[31]. Noble metal based catalysts promote hydrogenation and hence form cycloalkanes as well as C1-C2 light hydrocarbon due to hydrogenolysis[32].

Oxide materials, by virtue of their Lewis acidity, are reported to promote acid catalyzed reactions such as isomerization and transalkylation which result in different isomers of alkyl aromatics such as all isomers of xylene or xylenol. These materials also catalyze dehydration reactions which are important for removal of the hydroxyl group of phenolics to form aromatics or cycloalkanes[26][24].

Metal catalysts are reported to catalyze DDO (hydrogenolysis) or HDO (ring hydrogenation). Direct deoxygenation (DDO) consists of removal of the phenolic –OH group by hydrogenolysis (which is a metal catalyzed reaction). It constitutes the removal of the hydroxyl substituent by hydrogenation, but without hydrogenation of the aromatic ring[10][22][33][34][32][35]. This results in aromatics (BTX) as final product. DDO as elaborated above is reported to takes place at relatively high temperature ranging up to 400°C[33] [35]. It involves direct cleavage of the C_{sp2}-O bond by hydrogenolysis. This reaction has a high energy barrier. Hydrodeoxygenation (HDO) on the other hand comprises of either partial[16][26] or complete hydrogenation[10][21][30][32] of the aromatic ring prior to removal of methyl or hydroxyl substituents[16][26][10][21] [30][14] Depending on the degree of hydrogenation of the ring, products range from cycloalkenes or cycloalkanes with or without alkyl substituents. Full ring hydrogenation forms corresponding (substituted) cyclohexanone and cyclohexanol which can further deoxygenate to (substituted) cycloalkanes. Full ring hydrogenation forming corresponding (substituted) cyclohexanone and cyclohexanol can further deoxygenate to (substituted) cycloalkanes. This mechanism predominates on noble metal catalysts at relatively low temperature 200-275°C and high pressure 50-200 bar[21] [30].

Keto-enol tautomerization is another mechanism which is proposed[5][15][22][36]. This consists of isomerization of the phenolic substrate to a keto isomer to yield corresponding cyclohexadienone which is partially hydrogenated to the corresponding cyclohexadienol. This is followed by dehydration to yield corresponding aromatic product. This requires bifunctional catalysis.

Hydrogenation (HYD) of m-cresol leads to oxygenated products such as methyl cyclohexanone and methyl cyclohexanol. Phenol intermediate can also similarly form the corresponding unsubstituted cyclic ketone and alcohol. Further deoxygenation of these cyclic oxygenates leads to formation of cyclic saturates such as cyclohexane and methyl cyclohexane.

Elaborate mechanisms involving formation of methyl cyclohexanol which dehydrogenates to corresponding aromatics is also proposed.

Thus, combination of active metal and support give rise to situations wherein certain combinations of the above reactions predominate.

Direct Hydrogenolysis of the Ar-OH bond by the metal to form toluene from m-cresol is also reported[37][33]. Demethylation of the methyl group or hydrogenolysis of the C_{ar}-O(H) bond of m-cresol[33] to form phenol or toluene followed by ring hydrogenation to cycloalkanes[34] is also reported. C_{ar} represents aromatic carbon.

The various mechanisms reported in literature converge into two major routes i) hydrogenation of the aromatic ring followed by deoxygenation (HDO). The hydrogenation gives rise to cyclohexanone which undergoes further hydrogenation of the C_{ar}=O to form cyclohexanol. These products are saturated cyclic oxygenates. These cyclic oxygenates undergo deoxygenation either by direct cleavage of the C_{ar}-O(H) bond or by dehydration of cyclohexanol. This results in cyclic saturates (cyclohexane/substituted cyclohexane) as products. ii) The partial hydrogenation of the aromatic ring at position adjacent to the C_{ar}-O(H) bond followed by deoxygenation or dehydration[26]. This results in aromatic products. This route includes variants such as direct cleavage of the C_{ar}-O(H) bond[33][35]. DDO is also reported to occur by enol-keto tautomerization[15][31][5][29][24] (which forms an unsaturated ketone through internal reorganization of the molecule) followed by hydrogenation of C=O to form an unsaturated cyclic alcohol which further dehydrates. Both routes result in the formation of aromatics (BTX) as products. The dehydration requires an acidic support or an oxophilic active phase as promoter[6]. Oxophilic catalytic materials favor hydrogenation of the C_{ar}-O(H) bond rather than hydrogenation of the aromatic ring[6]. The direct cleavage has a high energy barrier[26][6][24] hence possible only at high temperature 350-450°C.

Hydrogen consumption, and reaction conditions such as high pressure are important considerations. Partial hydrogenation, tautomerization or direct hydrogenolysis routes to form aromatics require less hydrogen than the routes which involve complete hydrogenation of the aromatic ring to cycloalkanes or cycloketones or cycloalcohols[38][14][33].

These reactions culminate in value addition to oxygenated products such as cyclic ketones (cyclohexanone), cyclic alcohols (cyclohexanol), phenols, xylenols or non-oxygenated products such as aromatics (BTX), cycloalkanes, cycloalkenes with or without side substituents depending on the reactant. Methane is formed by dealkylation or hydrogenolysis of methyl side chains and C1-C6 aliphatics by cracking reactions[32].

A number of studied are reported at high conversion (> about 40%)[16][10][21][23]. While, high conversions are desirable from productivity standpoint (determining yields of desired products), there can be difficulties in identifying intermediate products in a network of reactions such as in hydrodeoxygenation. Some studies are reported in batch reactor[21][38][39]. A reason for this could be the high residence time (low space velocity in flow reactors) to achieve high conversion. It is not clear whether the non-condensable product is accounted for in this case. Majority of the studies which are reported are carried out in flow reactors[15][16][26][8][10][22][37][6][23][25][24]. This is understandable from productivity standpoint because the latter have higher productivity than batch reactors.

Use of zirconia-alumina composites prepared by deposition precipitation is not reported for this reaction. Both these oxides have Lewis acidity and are oxophilic in nature. Alumina has some Bronsted acidity in addition to Lewis acidity. Similarly, studies using transition metals Co, Ni and Cu as active metals are fragmented because of which a direct comparison between these three cannot be made. As elaborated in chapter 4, Cu has electronic properties which are different from those of Co and Ni. Thus a study encompassing Co, Ni or Cu supported on zirconia-alumina bicomponent supports would be interesting.

In this work the hydrodeoxygenation of m-cresol is studied at low conversion 3-10%, in continuous flow vapor phase fixed bed reactors with the objective of identifying reaction pathways. A set of bifunctional catalysts comprising Ni, Co or Cu supported on a set of bi-component zirconia-alumina carriers with ZrO_2: Al_2O_3 varying from 1:0 to 0:1 are explored. m-cresol was used as a model compound to represent phenolic compounds derived from lignin. The conversion and product selectivity is correlated with physico-chemical characteristics of the catalysts.

5.2 Experimental

The zirconia-alumina supports were prepared by deposition precipitation of zirconia on alumina as per procedure shared in chapter 4. Briefly, zirconia was precipitated from an aqueous solution of its oxynitrate onto a powder of γ-Al_2O_3 using an aqueous solution of sodium carbonate.

The precipitation was carried out at 60°C. The precipitate was aged in the mother liquor for 1h prior to washing with hot demineralized water (80°C) till the sodium content was <500 ppm. It was dried and calcined at 550°C, 8h. The above carriers were impregnated with aqueous solutions of nitrates of Ni, Co or Cu by incipient wetness method (details in chapter 4). The samples were dried and calcined at 500°C. These sample were sized to a particle size fraction of 0.5-0.8 mm and used for the reaction in crushed particle tests.

The catalyst samples were characterized by N_2 physisorption, XRD, NH_3-TPD, TPR, XPS and Raman spectroscopy. Detailed of the methods and results of characterization of these samples is provided in chapter 4. Briefly zirconia had a strong influence on multiple characteristics. Increasing zirconia content led to i) decrease in specific surface area and pore volume (N_2 physisorption) ii) decrease in acidity (NH_3 TPD) iii) absence/decrease of active metals in surface layers (XPS) iv) larger crystallite size of active metals Co and Ni but smaller crystallite size of Cu (XRD) v) preferred orientation of 111 and 220 planes in the case of Cu and Co catalysts respectively vi) increased hydrogen spillover (TPR). TPR indicated that Ni has stronger interaction with alumina whereas Cu shows stronger interaction with zirconia. Co showed intermediate metal-support interaction with zirconia.

A fixed bed quartz reactor was used for the hydrodeoxygenation study. 2.2 g catalyst (0.5-0.8 mm) was charged to the reactor and reduced at 500°C for 4h with pure dry H_2 (300 ml/min). The catalyst was cooled to 350°C in H_2. m-cresol was fed at 4.4 g/h. Space time was 0.5 h on weight basis or 54 g cat h mol^{-1} m-cresol. H_2/m-cresol was maintained at 11.5 (molar), pressure was close to atmospheric. Product was condensed by circulating aqueous mixture of ethylene glycol at 5°C in the jackets of the condenser and gas-liquid separator. Samples were collected at 60 min on stream. Both the condensable and non-condensable products were measured and analyzed by Gas Chromatography using a 60 mm x 0.25 mm ID INNOWAX capillary column coupled to an FID detector. Pure compounds were used to identify reaction products by matching retention time. Phenol and xylenol was identified by GC-MS using a Perkin-Elmer Autosystem XL GC with Turbomass with quadrupole analyser with prefilter, Mass range 20-600 Daltons (amu), EI/CI mode. Material balance achieved was better than 93 wt%.

5.3 Results and discussion

5.3.1 Acidity by NH_3 TPD

The trend of strong and total acidity and acid strengths of the catalysts determined by NH_3 TPD is shown in Figures 5.1 and 5.2 below. Catalyst names starting with ZA-## are those of supports. ## stands for the bulk molar concentration of zirconia in the support expressed as percent. Catalyst names starting with Ni-ZA ## or Co-ZA ## or Cu-ZA ## are those of supported metal catalysts where ## represents zirconia content in the support of these catalysts expressed as mole percent.

As seen from Figure 5.1 both strong and total acidities increase with decreasing zirconia content, both for the supports and the catalysts. In case of the supports, strong acidity sort of stabilizes/plateaus when zirconia is decreased below 50 mole%.

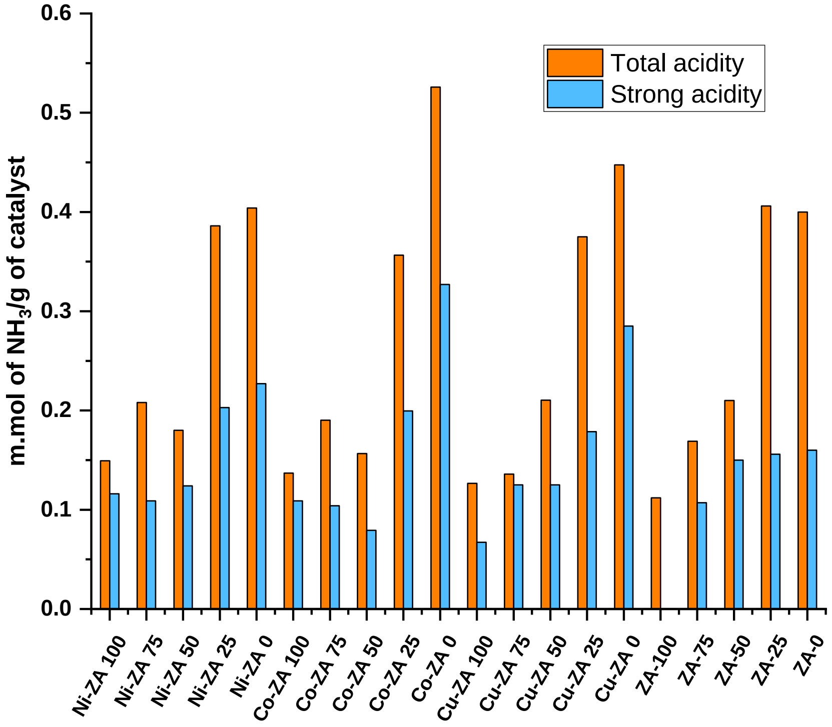


Figure 5. 1: Strong and total acidity of catalysts and supports by NH_3 TPD

In the case of the catalysts a sharp increase in acidity (relative to the support) is seen when the zirconia content decreases below 50 mol%. The increase in the case of carriers (at 50 mol% zirconia) appears to be related to strong interaction or formation of solid solution between zirconia and alumina which is supported by XRD (chapter 3, Figure 3.2). An alternative is shrinkage of zirconia which results in increase in the exposure of alumina. XPS results which show 60% lower zirconia on the surface than what is expected for the bulk composition for samples with 1:1 ZrO_2:Al_2O_3 (molar) supporting the shrinkage hypothesis.

Comparing the acidities of supports with that of the catalysts in Figure 5.1, it is observed that neat zirconia (ZA-100) does not present any strong acidity, whereas all three supported metal catalysts based on this carrier show strong acidity. This acidity arises from Lewis acidity of the oxides of the active metals. The value is 0.10-0.11 mmol NH_3/g cat for Co-ZA 100 and Ni-ZA 100 catalysts whereas it is about half this vale (0.067 mmol NH_3/g cat) for Cu-ZA 100. In the M-ZA 75 series of catalysts (where M = Co or Ni or Cu) it is observed that strong acidity is comparable with that of the support ZA-75. In the case of M-ZA 50 catalysts the acidity of Ni-ZA 50 and Cu-ZA 50 are slightly lower than that of support ZA-50 (0.125 mmol versus 0.15 mmol NH_3/g cat). The acidity of Co-ZA 50 is significantly lower 0.079 mmol NH_3/g cat. In case of M-ZA 25 acidity of all three catalysts is higher than that of support ZA-25. Trend is Ni-ZA 25 ~ Co-ZA 25 > Cu-ZA 25. In the case of M-ZA 0 too strong acidity is higher than that of support ZA-0 for all three catalysts but the trend is different Co-ZA 0 > Cu-ZA 0 >> Ni-ZA 0.

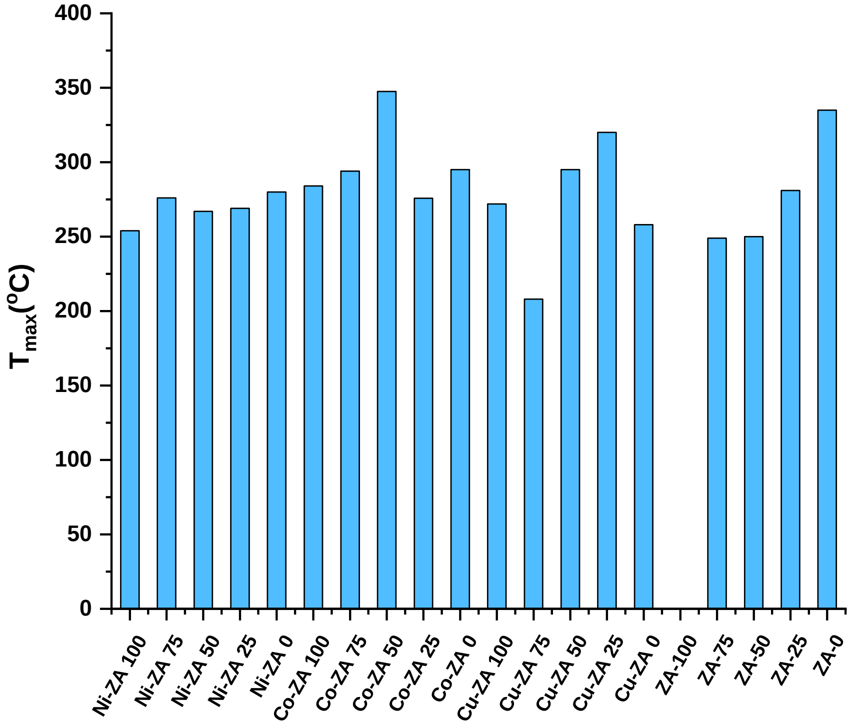


Figure 5. 2: Acid strength of catalysts and supports by NH_3 TPD

As seen from Figure 5.2, acid strength (which is expressed as the peak temperature of desorption of ammonia from the surface of the catalyst) increases with decreasing zirconia content of the support in case of the supports. Nickel series of catalysts also shows a similar trend. However, Ni-ZA 25 and Ni-ZA 0 show lower acid strength than that of their corresponding supports. Amongst Co series of catalysts, acid strength increases with decreasing zirconia content till Co-ZA 50 after which there is an abrupt decrease in the case of Co-ZA 25 and Co-ZA 0. Like the Ni series the acid strength in the latter two is lower than that of their corresponding carriers. In the case of Cu series excepting for Cu-ZA 75, the catalysts from Cu-ZA 100 to Cu-ZA 25 show an increasing trend in acid strength with decrease in zirconia content. Cu-ZA0 again shows a decrease. The acid strength of Cu-ZA 75 and Cu-ZA 0 is lower than that of their corresponding supports.

5.3.2 X-ray Diffraction

Results of XRD crystallite size of fresh calcined catalysts and corresponding reduced catalysts used for HDO of m-cresol are shown in Figure 5.3 below.

As seen from results in Figure 5.3, the crystallite size of CuO in calcined Cu catalysts increases with decreasing zirconia content of catalyst. The reduced catalysts too show a similar trend for Cu.

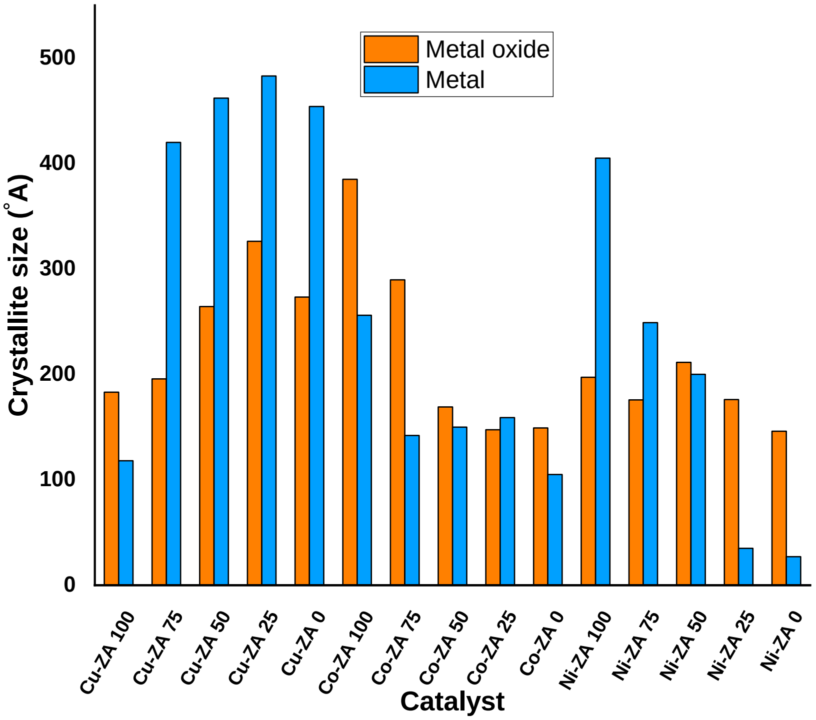


Figure 5. 3: Crystallite size of the final catalysts

The behavior of calcined catalysts correlates with the Tmax of H_2-TPR (Figure 3.14 Chapter 3) which shows that CuO has stronger MSI (metal support interaction) with zirconia than with alumina. Thus Cu-ZA 100 (neat zirconia support) shows least sintering and hence smallest crystallite size amongst Cu series of catalysts. Excepting for Cu-ZA 100 (where support is neat zirconia), the crystallite size of Cu^0 (in reduced catalyst) in all the other catalysts is significantly larger than that of the corresponding CuO crystallites in the calcined catalyst indicating further sintering/agglomeration during reduction. Thus, Copper tends to sinter to a larger extent during reduction as the zirconia content of catalyst decreases.

In contrast, the crystallite size of oxides of Co and Ni (calcined catalysts) decreases with decreasing zirconia content. The change in crystallite size of CoO with decrease in zirconia is significantly larger than that of NiO. Crystallite size of Co^0 also decreases with decrease in zirconia content of support. Crystallite size of NiO decreases with decreasing zirconia content. Crystallite size of Ni^0 also shows a decrease with decreasing zirconia content. But Ni-ZA 100 and Ni-ZA 75 show increase in crystallite size of Ni^0 over their corresponding oxides, similar to Cu^0 with lower zirconia content (Cu-ZA 75 to Cu-ZA 0). The trends of Co and Ni catalysts supported on carriers with different zirconia content corroborates with results of H_2-TPR (Figures 3.14 a, b, Chapter 3) where it is seen that Ni has strong MSI with alumina and Co has MSI behavior which is intermediate between that of Cu and Ni. All the reduced Co catalysts show crystallite size of Co^0 which is smaller than or equal to that of the corresponding oxide indicating that there is no further sintering during reduction. Co-ZA 0 shows a significantly smaller crystallite size upon reduction. Calcined Ni catalysts also show a decrease in crystallite size with decreasing zirconia content similar to Co catalysts because of stronger interaction of NiO with alumina of the support, which retards sintering.

The melting points of the three oxides are CoO 1935°C, NiO 600°C, CuO 1326°C. NiO has a significantly lower melting point than the other two oxides and its Tamman (0.5 times melting point in K) and Huttig (0.3 times melting point in K) temperatures, which are indicators for onset of metal particle/atom migration on the surface of the support, are 436K and 262 K respectively. These are well within the calcination temperature 773 K of these catalysts in the current study. This can either lead to redispersion or agglomeration based on the metal loading and importantly the extent of metal support interaction (as seen in the case of the Ni-ZA series of catalysts upon their reduction).

Upon reduction Ni-ZA 100 and Ni-ZA 75 (high zirconia content) show an increase in crystallite size of Ni^0 (reduced catalyst) relative to their oxides (calcined catalyst) indicating further sintering during reduction. Based on results of TPR (Figure 3.14 Chapter 3) this is attributed to poor interaction of Ni with zirconia/zirconia rich carrier. Ni catalyst with 50 mol% zirconia (Ni-ZA 50) does not show a decrease in crystallite size relative to the calcined catalyst upon reduction.

Interestingly, and contrary to nickel catalysts with zirconia ≥75 mole%, Ni-ZA 25 and Ni-ZA 0, with zirconia content 25 mole% and 0 mole% (neat γ-alumina) show a significant decrease in the crystallite size Ni^0 upon reduction. This is only possible if the nickel undergoes re-dispersion during reduction in these catalysts. Similar increase in dispersion (redispersion) has been reported for Nickel on alumina and silica supports[40][41]. Phichitkul[41] have reported redispersion of NiO on zirconia and α-Al_2O_3 supports during reduction. He reports redispersion of nickel after reduction with resultant increase in metal surface area for catalysts which are pre-calcined at high temperature. The increase in nickel surface area is attributed to fracture of NiO particles upon reduction to Ni^0 due to a 40% decrease in volume, resulting in migration of the particle along the metal-support interface to relieve strain energy between tensile stress on the Ni particle and compressive stress on the support. He further states that strong bonding between metal and support is necessary for this to happen. The strong interaction between nickel and alumina is evident in TPR studies of the current work. Nakayama et.al[40] have reported similar behavior for thin film of NiO on Al_2O_3 and SiO_2. They too attribute the increase in metal surface area to fracture of existing metal particles. The melting points of the metals, (with Huttig temperature in braces), are Co 1085°C (407 K), Ni 1455°C (518 K) and Cu 1495°C (530 K). The Huttig temperatures are lower than the reduction temperature used in our study (773 K), hence these metals are amenable to redistribution/agglomeration. Further, the reduction environment strongly influences agglomeration. In presence of H_2 (reducing agent) and/or moisture many metals are known to be prone to sintering during reduction[42].

Thus, the results corroborate with those of temperature programmed reduction (TPR) of these catalysts which show that metal support interaction (MSI) with alumina decreases in the order Ni > Co> Cu. Cu shows strong MSI with zirconia. MSI helps to achieve better dispersion by binding the active metal to the support and minimizing agglomeration during calcination and use.

5.3.3 X-ray Photoelectron Spectroscopy (XPS)

The surface concentration of active metals (represented by XPS peak area) is plotted against zirconia content of the catalyst in Figure 5.4.

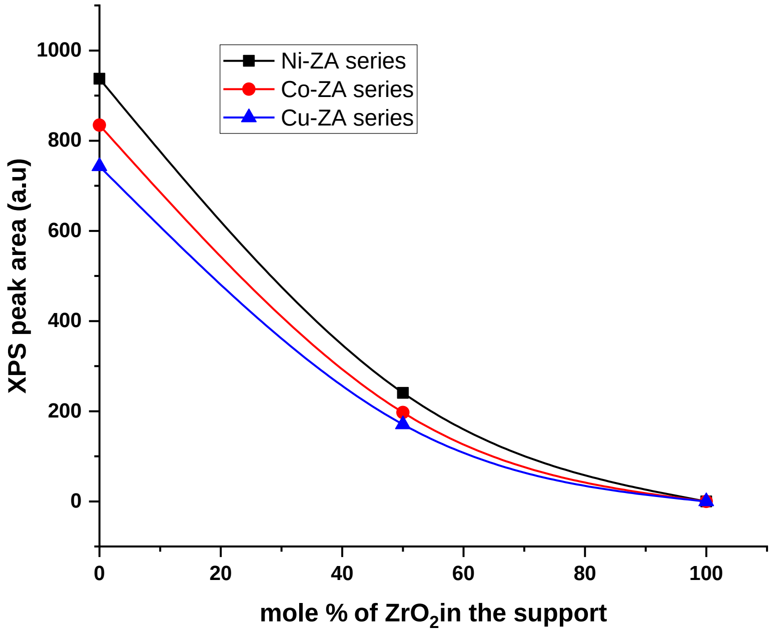


Figure 5. 4: Peak area of active metals by XPS

As observed from Figure 5.4, the surface concentration of active metal (represented by peak area) decreases with increasing zirconia content of the catalyst. Active metals are not detected on the surface of M-ZA 100 series (neat zirconia support). This is expected to affect metal function of the catalyst.

5.4 Deoxygenation of m-cresol

5.4.1 Conversion

Trend of conversion of m-cresol with change in carrier composition is shown in Figure 5.5 below

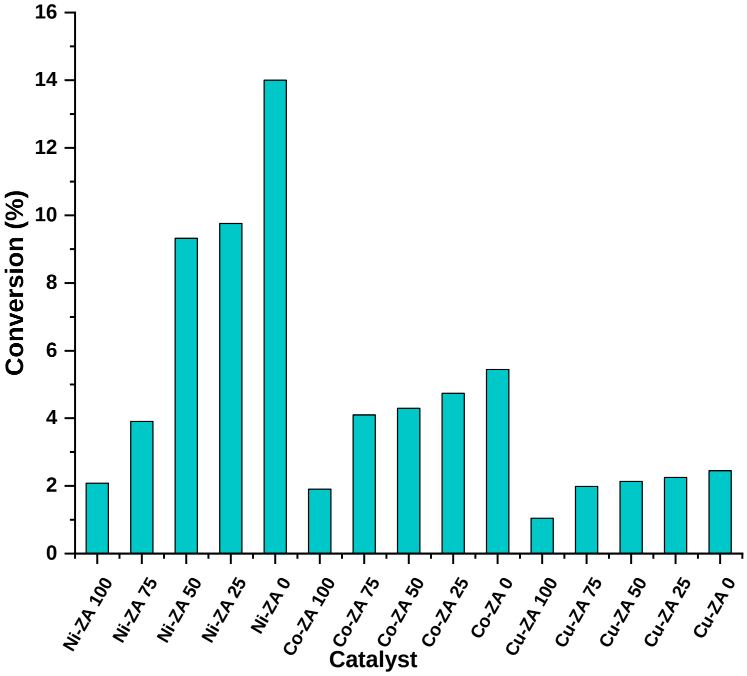


Figure 5. 5: Trend of conversion of m-cresol

As seen from Figure 5.5, conversion of all the catalysts increases as the zirconia content of the catalyst decreases. This correlates with an increase in the surface concentration of these active metals with decreasing zirconia (Figure 5.4) for all the catalysts and a decrease in their crystallite size with decreasing zirconia content of catalyst (for Co and Ni) as determined by XRD (Figure 5.3 above). It is noted that acidity also increases as zirconia content decreases (Figure 5.1). This favors acid catalyzed reactions like disproportionation of m-cresol or deoxygenation of phenolics via the tautomerization or partial ring hydrogenation mechanism. Nickel catalysts Ni-ZA 0 and Ni-ZA 25 show the highest conversion. They also show smallest XRD crystallite size (Figure 5.3 above). Thus conversion of m-cresol is dependent on crystallite size of the active metal, surface concentrations of active metals and acidity.

All three catalysts supported on neat zirconia (ZA-100) show poor activity. This is irrespective of the active metal Co, Ni or Cu. This correlates with results of XPS (Figure 5.4 above) which show that surface concentration of active metals is below detection limit in these catalysts. The active metals are either located in subsurface regions or significantly agglomerated. Acidity is also low which affects tautomerization reactions. Yang et.al.[32] have studied size dependence of Ni crystallites on hydrodeoxygenation of m-cresol over Ni/SiO_2 catalysts. They report a conversion of 9% at 300°C, 1 atm, 0.5 h (W/F) for catalysts with 22.1 nm Ni crystallite size as determined by XRD. The XRD crystallite of Ni catalysts of current study varies from 14.6 to 21.1 nm and conversions around 7-14% are observed for alumina rich catalysts which are in the same ballpark range.

5.4.2 Product Selectivity

Major products observed were phenol, xylenol, cyclohexane, benzene, and toluene. Cyclohexene was clubbed with cyclohexane. Small quantities of cyclohexanone and cylohexanol were also detected. The selectivity of their methyl substituents was between 2-8 and 2-5 % respectively.

Conversion of m-cresol was largely between 2-8% for almost all samples (Figure 5.5). Product selectivity across the catalysts is compared in the results below.

Trend of selectivity to phenol and xylenol is shown in Figure 5.6. They were amongst the major products observed in this study. Disproportionation of m-cresol is reported for Ga-BEA[25], Pt-H-BEA[24], HZSM-5[43] and USHY[23]. Products are xylenol and phenol. Formation of xylenol by disproportionation is also reported on Ni/SiO_2 catalysts[32]. Unreduced NiO is stated to provide Lewis acidity necessary for the reaction in that case.

From Figure 5.6, within a specific metal series, catalysts which are rich in zirconia show higher xylenol than those which are rich in alumina. This is irrespective of the type of active metal. Comparing the trend of acidity (Figure 5.1) it is observed that zirconia rich catalysts have relatively low acidity. Further comparing the acidity of supports (ZA-0 to ZA-100) and calcined supported metal catalysts (M-ZA-# where M= Co, Ni, Cu), it is observed that while neat zirconia support (ZA-100) does not show any strong acidity, the corresponding supported metal catalysts (M-ZA 100) show significant strong acidity. This increase in acidity is due to Lewis acidity originating from the metal oxides of the active metals. From results of TPR (Figure 3.14 a,b,c; Chapter 3) it is observed that not all the metal oxide reduces at 500°C. Thus, some residual unreduced oxide remains and lends Lewis acidity to the reduced catalysts. From Figure 5.6 it is also observed that trend of active metals for selectivity to xylenol of zirconia rich catalysts (ZA-100 series) is Cu>Ni>Co. It appears that an increase in acidity beyond that of M-ZA 100 catalysts shifts the selectivity from disproportionation to tautomerization of m-cresol which forms toluene (Figure 5.12).

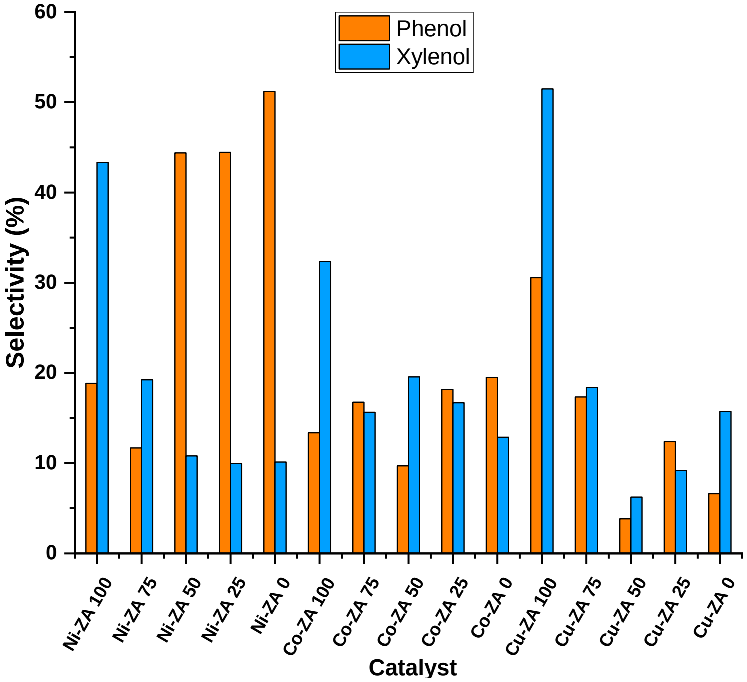


Figure 5. 6: Trend of selectivity to xylenol and phenol.

The ratio of selectivity of phenol to xylenol is shown in Figure 5.7 below.

As seen from Figure 5.7, the ratio of phenol:xylenol largely ranges between 0.56 – 1.4 for catalysts containing > 50 mol% zirconia (irrespective of active metal). Catalysts from Ni-ZA 50 to Ni-ZA 0 show a significantly higher ratio. The stoichiometric ratio on weight basis is 0.77. Considering that these are intermediates which react further to other products the ratio can be considered in ballpark range of the stoichiometric value. Thus, it is reasoned that they form by the disproportionation of m-cresol.

$$2 \text{ m-cresol} = \text{Phenol} + \text{Xylenol} \qquad \text{Equation 12}$$

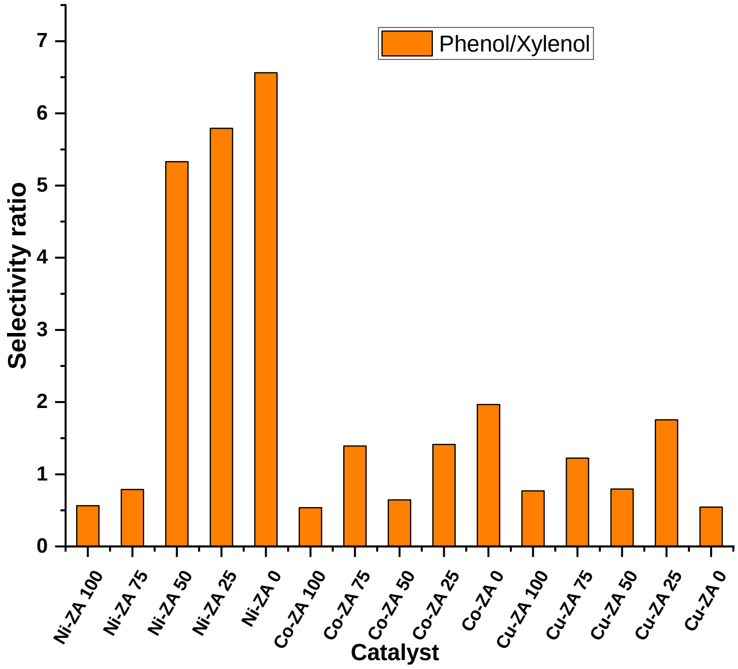


Figure 5. 7: Weigh ratio of phenol/xylenol

Further, from Figure 5.7 nickel catalysts containing ≥50 mol% alumina (lower zirconia) show significantly higher phenol relative to xylenol (phenol:xylenol weight ratio 4-6.5) than all the remaining catalysts which contain <50 mole% alumina (higher zirconia). Such high ratio is not possible unless the additional phenol forms from a different route. In these cases it appears that phenol is formed by the dealkylation or hydrogenolysis of m-cresol in addition to its disproportionation. These catalysts also show more methane (Figure 5.8 below) which corroborates with the above hypothesis. Demethylation can take place by either acid catalysis or metal catalyzed hydrogenolysis. Such mechanisms are reported in literature[33][34][32][35]. Demethylation is difficult to achieve with Lewis acidity at the reaction conditions used in the current work (350°C atmospheric pressure), whereas Nickel is well known for its hydrogenolysis activity: Hydrogenolysis of xylene to toluene and benzene is reported to take place on Nickel/Kieselguhr supported catalyst at 280-340°C, H_2/HC 2.1-2.3, space velocity 0.44, atmospheric pressure, 60-70%[44]. Reaction conditions are similar to those used in the current study. Thus, it is reasoned that the additional phenol forms by hydrogenolysis of methyl group of m-cresol on Ni catalysts which are supported on carriers containing ≤50 mole% zirconia.

These samples have a smaller crystallite size (Figure 5.3) and higher acidity (Figure 5.1) than the remaining Ni catalyst samples. Further, it is also interesting to note that the hydrogenolysis reaction in Ni catalysts is significantly suppressed when zirconia content of the carrier is >50 mol% (Ni-ZA-100 and Ni-ZA 75). As seen from Figure 5.3 these samples show larger crystallite sizes than the other samples and low acidity (Figure 5.1).

Non-condensable product CH_4 is reported to form by hydrogenolysis of the methyl group of m-cresol[33][45][32][35]. The selectivity to CH_4 is shown in Figure 5.8 below.

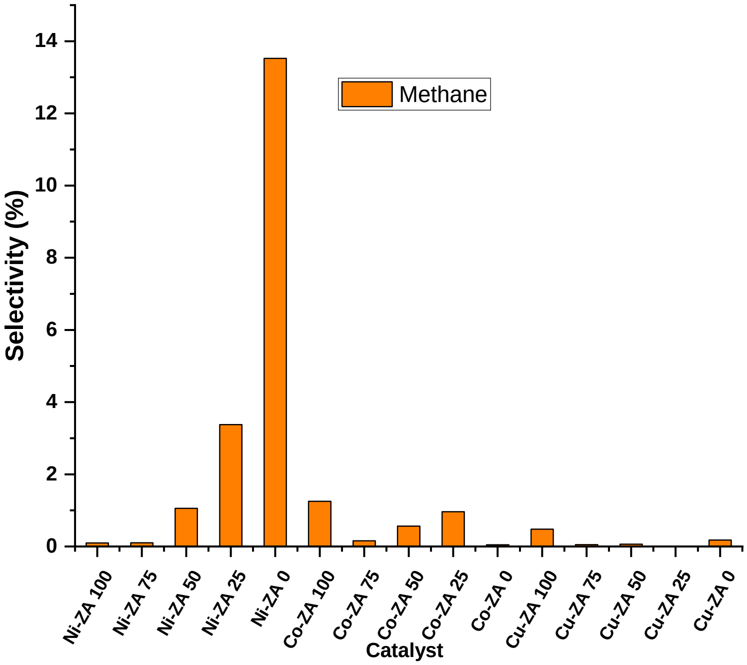


Figure 5. 8: Selectivity to CH_4

As seen from Figure 5.8, Nickel catalysts with zirconia ≤50 mole% in their carrier and relatively high acidity and small particle size show significantly higher selectivity to CH_4 than the remaining catalysts. However, the quantity of CH_4 is in stoichiometric excess of phenol especially in the case of Ni-ZA 25 and Ni-ZA 0. Hence, some CH_4 appears to form by some other route such as cracking in addition to (hydrogenolysis of methyl group of m-cresol). Ni-ZA 0 has the highest acidity in the Ni-ZA series, which is an important property for cracking.

Benzene is also observed as another major product. Trend of benzene selectivity for the various catalysts is given in Figure 5.9 below

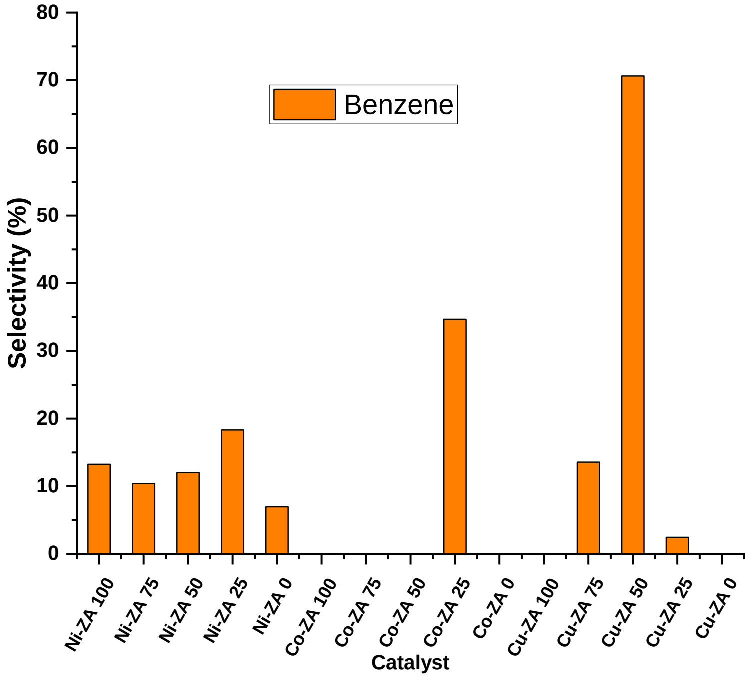


Figure 5. 9: Trend of selectivity to Benzene

Between the active metals, cobalt and copper catalysts supported on carriers with 25 and 50 mol% zirconia respectively (lower zirconia) show significantly higher selectivity to benzene than corresponding Ni catalysts. They also stand out within the respective active metal series.

Catalysts which are relatively rich in alumina (Cu-ZA 50 and Co-ZA 25) show significantly higher selectivity to benzene in case of Co and Cu catalysts. Whereas benzene is formed in very small quantities when the zirconia content is higher or lower (≥75% or ≤25 mol%) in these catalysts. However, the Ni catalysts show benzene across the entire composition range than their Co or Cu counterparts. Albeit lower in concentration. The nickel catalysts show a slight increase in selectivity to benzene with decreasing zirconia content (increasing acidity) with maxima at Ni-ZA 25. This is consistent with the mechanism of formation of benzene from phenol by tautomerization or partial hydrogenation followed by dehydration. Acidity is necessary for dehydration. This is elaborated below. As seen from Figure 5.3 XRD crystallite size of Co^0 and

Ni^0 catalysts decreases with decreasing zirconia whereas acidity (Figure 5.1) and surface concentration of active metals (Figure 5.4) increase. Thus, the combination of metal and support (acid) function appears to be important for formation of benzene. This combination appears to be very specific for Co and Cu catalysts compared to Ni catalysts for the formation of benzene.

Benzene can form either by DDO of phenol by tautomerization[15][36] route or partial hydrogenation[26] route, both of which are followed by dehydration of partially saturated cyclic alcohol. An alternative is the direct hydrogenolyis of the aromatic C_{ar}-OH group, where C_{ar} stands for aromatic carbon. This reaction is catalyzed by metal. This route has a high energy barrier[15]. Allison Robinson et.al.[6] have shown through DFT studies for m-cresol that direct deoxygenation (removal of the hydroxyl group) even after hydrogenation of the aromatic ring has a high energy barrier, whereas a tautomerization route is energetically more favorable. Significantly high reaction temperatures are required for the direct removal of the hydroxyl group from phenoics. Such direct DDO is reported for m-cresol on sulfided Mo/Al_2O_3 catalysts at 340°C[12] and on Pd/Fe_2O_3 up to 400°C[33] and for DDO of guaiacol over Pd-Fe/C catalysts[35].

Another route for the formation of benzene is the dealkylation of toluene by hydrogenolysis. Besides being energetically unfavourable, dealkylation of toluene to benzene is expected to form attendant methane. Comparing trends of Figure 5.9 with those of Figure 5.8 it is clear that there is no relation between non-condensable product (C1 product) and benzene formation. Thus, formation of benzene by the dealkylation of toluene is ruled out. Trends of selectivity of benzene and phenol are shown in Figure 5.10 below.

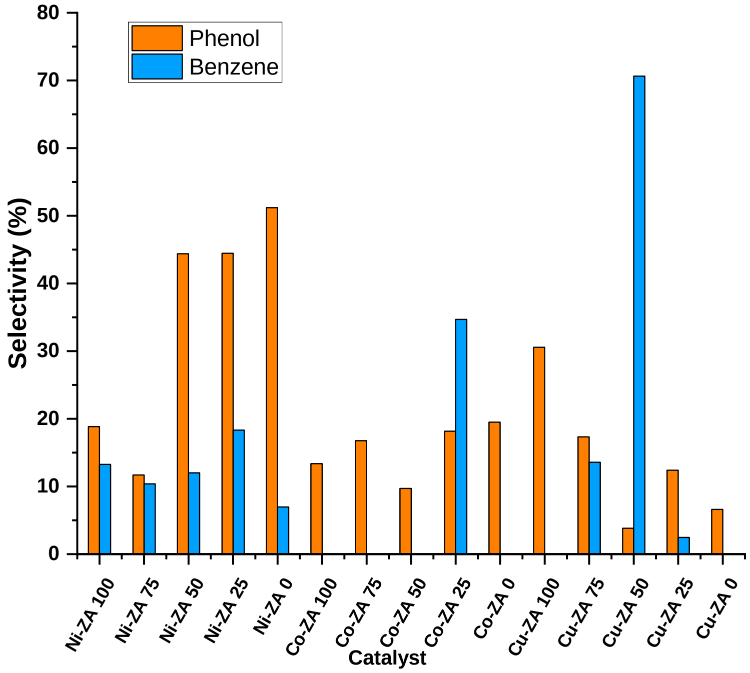
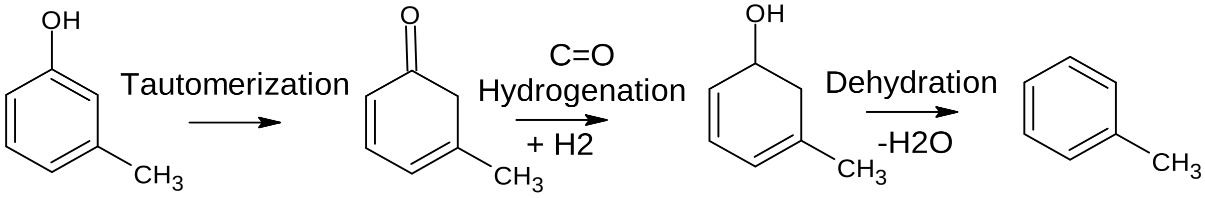


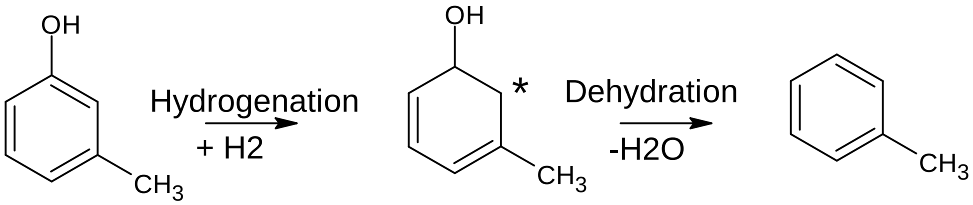
Figure 5. 10: Selectivity trend of benzene and phenol

As seen from Figure 5.10 selectivity to benzene shows a significant inverse trend with phenol. When selectivity of benzene increases, the selectivity of phenol drops. Based on the above discussion regarding high energy barrier for direct deoxygenation (dehydroxylation of phenol), and, considering that the current studies were carried out at 350°C at atmospheric pressure with relatively low H_2/m-cresol (11.5 molar), the energetically favorable routes of partial hydrogenation[26] or tautomerization proposed by Nei et.al.[5] and de Souza et.al.[15], appear to be more probable ones for the formation of benzene. The former involves partial hydrogenation of the ring C=C adjacent to C_{ar}-O(H) followed by dehydration whereas the latter involves enol-keto tautomerization of phenol to 3,5-dicyclohexadieneone which undergoes hydrogenation of the C_{ar}=O to the corresponding cyclohexadienenol. This is followed by dehydroxylation through dehydration to yield benzene. It is noted that bifunctionality (both metal and acid function) is necessary for both routes. Acidity increases with decreasing zirconia content. Surface concentrations of active metals also increases. Thus both factors are favorable for this mechanism as alumina content of catalyst increases. Thus, benzene appears to form from one of these mechanisms.

The schematic of Tautomerization as proposed by Lei et.al.[29] and de Souza et.al.[15] is given below. It forms aromatics as products.



The schematic of partial hydrogenation as proposed by Foster et.al[26]. is given in below. The aromatics can further undergo ring hydrogenation to form cyclic saturates.



Oxophilicity is reported to favor the tautomerization route. Cobalt is slightly more oxophilic (0.4) than both nickel and copper (0.2 each). That supports the high selectivity of Co-ZA 25 for benzene. However, since Cu-ZA 50 (which has lower oxophilicity than Co), also shows high selectivity to benzene, higher oxophilicity alone cannot be attributed to the higher selectivity of Co-ZA 25. Thus, it appears that a certain combination of metal and acid function is also important.

This aspect is also applicable to the selectivity to toluene, which appears to form by an analogous route from m-cresol.

Both cyclohexane (major quantity) and small quantities of cyclohexene (in some cases) were observed in the product. The two were clubbed together and reported since cyclohexene is ultimately expected to form cycloalkane.

The trend of selectivity to cyclohexane is compared with that of benzene in Figure 5.11 below. As seen from Figure 5.11 a clear inverse trend is evident between cyclohexane and benzene.

Also, from Figure 5.11 Ni and Co catalysts which are relatively rich in zirconia (100-75 mol%) show higher selectivity to cyclohexane relative to benzene. In the case of Cu catalysts the selectivity to cyclohexane peaks at zirconia content 25 mole% (lower zirconia content), which is different from that of Co and Ni.

Cyclohexane can form from one of two routes: i) hydrogenation of the aromatic ring of benzene which is earlier formed from phenol by tautomerization or partial ring hydrogenation of phenol followed by dehydration ii) HDO of phenol (ring hydrogenation) to cyclohexane via cyclohexanol. Direct formation from m-cresol requires demethylation of the methyl group in addition to the remaining reactions to form cyclohexane and is unlikely. It is also not supported by the selectivity trend of attendant CH_4 that should form (Figure 5.8).

Benzene and phenol show a nice inverse relationship (Figure 5.10), similarly, cyclohexane and benzene (Figure 5.11) also show a nice inverse trend. Selectivity to cyclohexane is higher on catalysts which are rich in zirconia in case of Ni and Co catalysts. Catalysts having at least some alumina component (M-ZA 75 or M-ZA 50) show better selectivity to cyclohexane irrespective of the active metal. The alumina imparts acid character which is required for formation of benzene by tautomerization of phenol. Hence, it is reasoned that cyclohexane is formed by the ring hydrogenation of benzene which in turn is formed by Tautomerization or partial hydrogenation of phenol. Requirement of bifunctionality for the latter reaction supports the higher selectivity of cyclohexane on catalysts containing alumina (which are more acidic than M-ZA 100 catalysts). Cu based catalysts show higher selectivity to cyclohexane than Co and Ni catalysts. As seen from results of TPD, Cu catalysts are the least acidic amongst the three series (Figure 5.1 above).

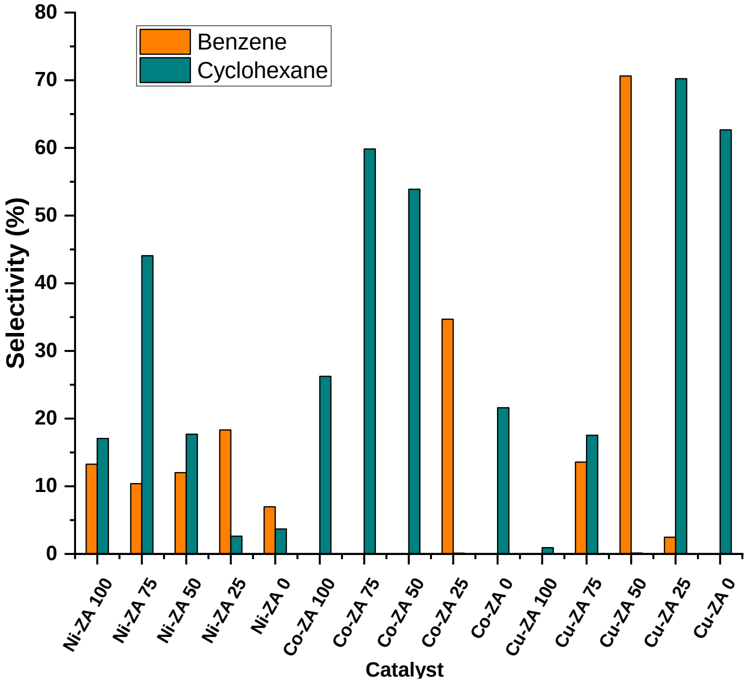


Figure 5. 11: Trends of cyclohexane and benzene

Thus, it is reasoned that cyclohexane is formed by the ring hydrogenation of benzene. It appears that a certain combination of metal and acid function is important for selectivity. Acidity between 0.08-0.125 mmol NH_3/g catalyst gives highest cyclohexane selectivity for Co and Ni catalysts whereas Cu catalysts require still higher acidity (0.15-0.16 mmol NH_3/g catalyst). Increasing acidity still further favors selectivity to aromatics rather than cyclic saturates in Co and Ni catalysts. Cu catalysts thus show a different trend.

Toluene is another major product which was observed in this work. Trends of selectivity to toluene are shown in Figure 5.12 below. The trend is Co-ZA 0 > Cu-ZA 75 > Ni-ZA 25.

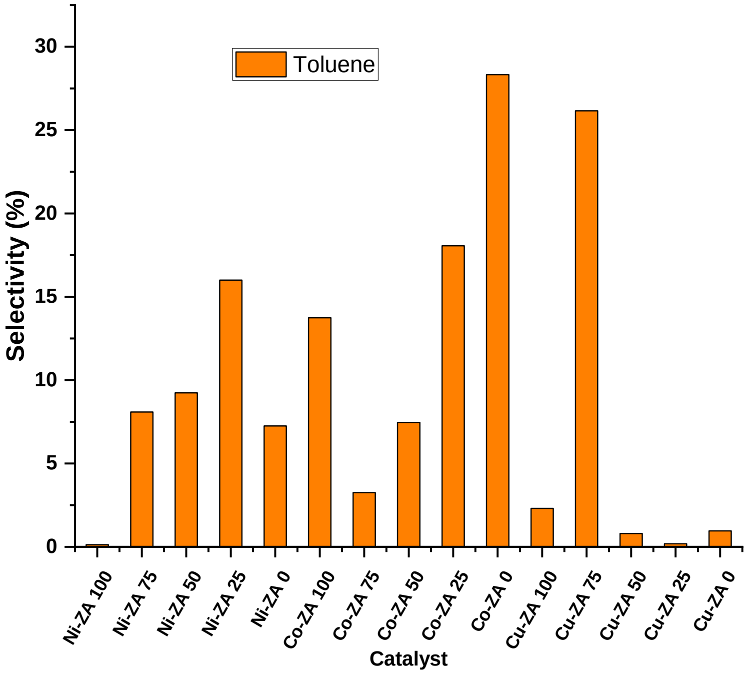


Figure 5. 12: Trend of selectivity to Toluene

Within Ni catalysts selectivity to toluene increases as the zirconia content of the catalyst decreases. Ni-ZA 0 is an exception. Ni-ZA 25 which has average Ni^0 particle size 34 Å shows highest selectivity to toluene within Ni catalysts. This catalyst also has high acidity. The trend of conversion and selectivity to toluene with particle size is consistent with studies of Yang et al.[32] who report that Ni/ SiO_2 catalysts give higher selectivity to toluene (from m-cresol) when the particle size of Ni is smaller (18-48 Å). SiO_2 has very little acidity compared to zirconia or alumina[46], hence the Lewis acidity is imparted by nickel oxide in that case. Interestingly, Ni-ZA 0 shows lower selectivity than Ni-ZA 25 although its particle size (Ni^0) is similar to that of Ni-ZA 25 (Figure 5.3). However, strong acidity of Ni-ZA 0 is higher than that of Ni-ZA 25 (Figure 5.1). It shows exceptionally high hydrogenolysis activity forming methane (Figure 5.8). Thus, acidity of the catalyst appears to matter as also seen in the case of selectivity to benzene and cyclohexane.

Within Co catalysts too selectivity to toluene increases with decreasing zirconia content. Co-ZA 100 is an exception. As seen from Figure 5.3 the XRD crystallite size of Co^0 also decreases with decreasing zirconia content. Co-ZA 0 which has the smallest XRD crystallite size (105 Å of

Co^0 amongst Co catalysts) shows highest selectivity to toluene not only within the cobalt catalyst series but across all the catalysts. Thus, Co catalysts show a similar behavior to Nickel with respect to relation between particle size and selectivity to toluene. Besides, Co has higher oxophilicity than Ni or Cu which is also reported to favour formation of Toluene as discussed earlier.

Within Cu catalysts, Cu-ZA 75 (higher zirconia content) is the only catalyst which shows good selectivity to toluene. Thus Cu catalysts consistently show a different behavior compared to Co and Ni catalyst, as also seen in earlier sections.

Toluene is reported to form either by the direct DDO (dehydroxylation/deoxygenation) of m-cresol by hydrogenolysis[45] of the aromatic C_{ar}-OH bond (which is energetically unfavorable) or by tautomerization[15][31] followed by hydrogenation of the C=O bond to form an unsaturated cyclic alcohol (such as methyl cyclohexadienol from m-cresol) followed by dehydration to form toluene. This is similar to the formation of benzene from phenol. Another mechanism is the partial hydrogenation of the aromatic ring adjacent to the C-O(H) bond followed by dehydration[26], which is proposed by Foster et.al.

It is noted that bi-functionality (both metal and acid function) is necessary for both mechanisms starting with either tautomerization or partial hydrogenation. Either of which mechanisms could be occurring. The current studies could not distinguish between the two. Acidity increases with decreasing zirconia content (NH_3-TPD, Figure 5.1), whereas the XRD crystallite size of the metals decreases (Figure 5.3). Surface concentrations of active metals also increases (XPS) with decreasing zirconia content (Figure 5.4). Thus, all these factors are favorable for these two mechanisms. It appears that a certain optimal combination of metal and acid function is necessary.

Oxophilic character is reported to subdue hydrogenation of aromatic ring and favor C=O activation by their interaction with this bond[36], therein promoting the tautomerization route in DDO (without ring hydrogenation) of m-cresol to toluene. Oxophilic promoter such as Mo (in Mo promoted Pt/ Al_2O_3)[31] is reported to favor DDO of phenolics resulting in aromatic products. The same reference cites other works such as NiFe or Ru/SiO_2 which behave in an analogous manner[31]. Both Fe and Ru are oxophilic in these cases.

The effect of oxophilicity of supports on DDO is reported by de Souza et.al.[47] Therein Pd/zirconia is reported to give higher selectivity of benzene in HDO of phenol than Pd supported on silica or alumina supports. The higher selectivity of the zirconia supported catalyst is attributed to the higher oxophilicity of zirconia relative to silica. They have not discussed the oxophilicity of alumina, which is actually as oxophilic as zirconia[46], but more acidic[47]. In the same study[47] the HDO of cyclohexanol shows that Pd/ Al_2O_3 gives highest selectivity to benzene. The reason for this is attributed to the higher acid site density of alumina relative to zirconia and SiO_2 in that order. It is reported that SiO_2 does not have measurable acidity. The authors conclude that either oxophilicity and/or acidity is important. (The actual contribution of oxophilicity is thus inconclusive). Results of conversion of m-cresol on Pt/H-BEA also show high selectivity to aromatics therein supporting the preceding statement regarding importance of acidity (BEA {beta zeolite} being highly acidic). Pei-Ju-Hsu et.al[48], in their studies of HDO of p-cresol over Ni promoted with oxophilic promoter conclude that competing hydrogenation function or reaction conditions favorable for hydrogenation affect the outcome of oxophilic promoters to the extent of changing the trend of product selectivity. Thus, a combination of metal function and acidity are important parameters. Oxophilicity could be a contributor but needs additional study to prove conclusively.

From Figure 5.12 of the present study, between the active metals, Cobalt supported on alumina (Co-ZA 0) shows significantly higher selectivity to toluene than its Ni or Cu counterparts. Oxophilicity trend for the active metals of the current study is Co 0.4 > Ni 0.2 > Cu 0.2[46]. This is consistent with the trend of toluene formation. However, Cu is less oxophilic than Co yet gives better selectivity to toluene than Ni catalysts (which has oxophilicity comparable to Cu). Both alumina and zirconia are equally oxophilic supports. A differentiating factor between the two is that alumina has highest acidity. Hence a right combination of metal function and acidity appears to be an important criterion for formation of toluene (aromatics). This also applies to the trend of aromatics (BTX) in Figure 5.13 below.

Selectivity to aromatics (generically BTX) is shown in Figure 5.13 below. Selectivity's of benzene and toluene were combined.

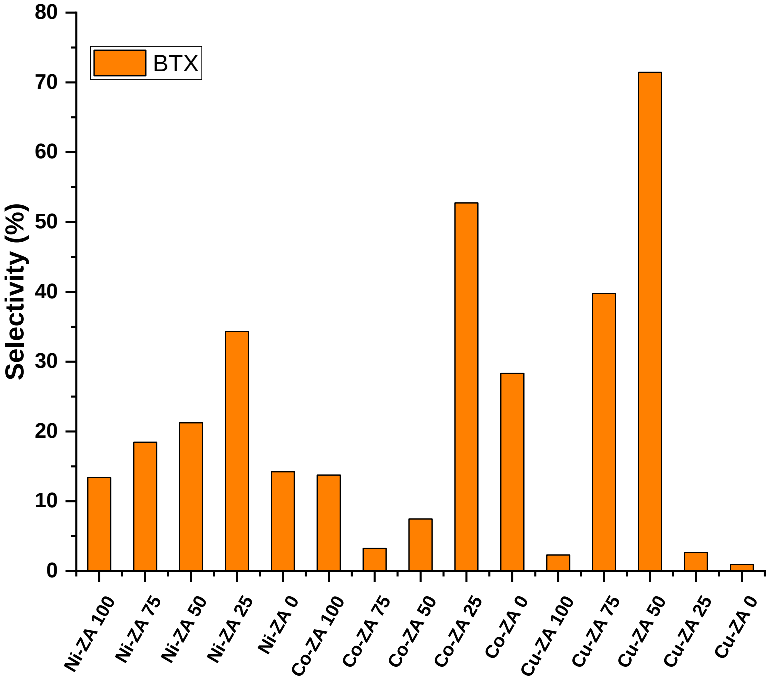


Figure 5. 13: Selectivity for formation of aromatics (Benzene+Toluene+Xylene)catalysts

Xylenes were not observed in the product. Hence further disproportionation of toluene did not occur on these catalysts.

From Figure 5.13 it is observed that Cu catalysts containing 50 mole% zirconia (Cu-ZA 50) and Co catalysts containing 25 mol% zirconia (Co-ZA 25) show significantly higher selectivity for BTX (aromatics) than the remaining catalysts. Ni-ZA 25 comes third. The trend of increasing acidity is opposite to this trend (Ni-ZA 25~Co-ZA 25 > Cu-ZA 50). Selectivity of these Co and Cu catalysts is significantly higher than for corresponding Ni catalysts. Within the Ni catalysts Ni-ZA-25 shows highest selectivity to BTX. Acidity of Ni-ZA 25 is not very different from that of Co-ZA 25 and higher than that of Cu-ZA 50 (Figure 5.1). Acid strengths too are not very different for the three catalysts. Hence the reason for low aromatics formation of Ni catalysts appears to be inherent to activity of nickel.

As mentioned above, Co is most oxophilic (0.4) and presents high aromatic selectivity. Ni has low oxophilicity (0.2)[46], which reflects in its lower selectivity to aromatics (and relatively higher activity for ring hydrogenation to aromatics). Cu although having low oxophilicity equal to

Ni (0.2) shows significantly higher selectivity to aromatics than Ni. Thus Cu presents a different behavior. It appears that certain combination of acid and metal function is important for DDO and this window is small in the case of copper and cobalt catalysts. Pei-Ju-Hsu et.al[48], in their studies of HDO of p-cresol over Ni promoted with oxophilic promoter conclude that competing hydrogenation function affects the outcome of oxophilic promoters. Our results are consistent with the observation of Pei-Ju-Hsu et.al.

The oxophilicity of the elements used as supports in the current study is Zr 0.8 and Al 0.8[46]. These elements are significantly more oxophilic than Co, Ni and Cu. While both Zr and Al have equal oxophilicity, metal support interactions with the active metals differ as determined by TPR. Ni shows strong MSI with alumina whereas Cu shows strong MSI with zirconia. Co presents intermediate MSI behavior. Based on the combination of metal and support those with moderate MSI show the highest selectivity to BTX in the current study. Huang et,al.[49] have studied Pt loaded on thin films of Nb_2O_5 or TiO_2 on $MgAlO_2$ catalysts for HDO of m-cresol. They report almost exclusive selectivity to toluene which is attributed to strong metal support interaction (SMSI). They support a tautomerization mechanism. Thus, metal support interaction could also be influencing the trends observed in the current study for formation of BTX.

Small quantities of methylcyclohexanone, methylcyclohexanol, (cyclic oxygenates) and methylcyclohexane were also observed as products. Cyclohexane was the major component amongst the cyclic saturates. This is consistent with reports that the presence of methyl substituents on the aromatic ring retards / hinders its hydrogenation[50].

As seen from discussion in the introduction section, the reactions comprising hydrodeoxygenation of phenolics can be divided into three major classes, viz.

- HYD (hydrogenation of aromatic ring without deoxygenation). Phenolics convert to cyclic oxygenates such as cyclohexanone, cyclohexanol (from phenol) and their methylated counterparts (from cresol). Thus products are cyclic oxygenates. This is a metal catalyzed reaction.
- HDO (hydrodeoxygenation of phenolics). Here the cyclic oxygenates formed by HYD undergo deoxygenation to form cycloalkanes (cyclic saturates) viz. cyclohexane and methylcyclohexane from phenol and cresol respectively. Ring hydrogenation of aromatics (formed from phenolics) is also included. Both are metal catalyzed reactions.

- TAU (either tautomerization or partial hydrogenation of phenolics followed by dehydration). This proceeds by partial hydrogenation of the aromatic ring adjacent to the Car=O bond or by tautomerization of phenolics leading to partially hydrogenated cyclic oxygenates. The latter undergo dehydration leading to the formation of aromatics, viz. Benzene, toluene and xylene. This requires bifunctional catalysis – combination of metal and acid function.
    - Technically aromatics can also hydrogenate to cyclic saturates.
    - It is not possible to distinguish between relative extents of hydrogenation of aromatics to cyclic saturates and HDO of cyclic oxygenates to cyclic saturates, hence they are clubbed together under HDO.
- Metal functions can also catalyze demethylation or dehydroxylation by direct hydrogenolysis.
- Acidity of the catalysts can also result in disproportionation, transalkylation, demethylation and cracking.

Trends of selectivity of HYD, HDO and TAU are shown in Figure 5.14 below.

As seen from Figure 5.14, trends for TAU (aromatics) and HDO (cyclic saturates) largely show an opposite trend. Where one peaks the other drops into a valley.

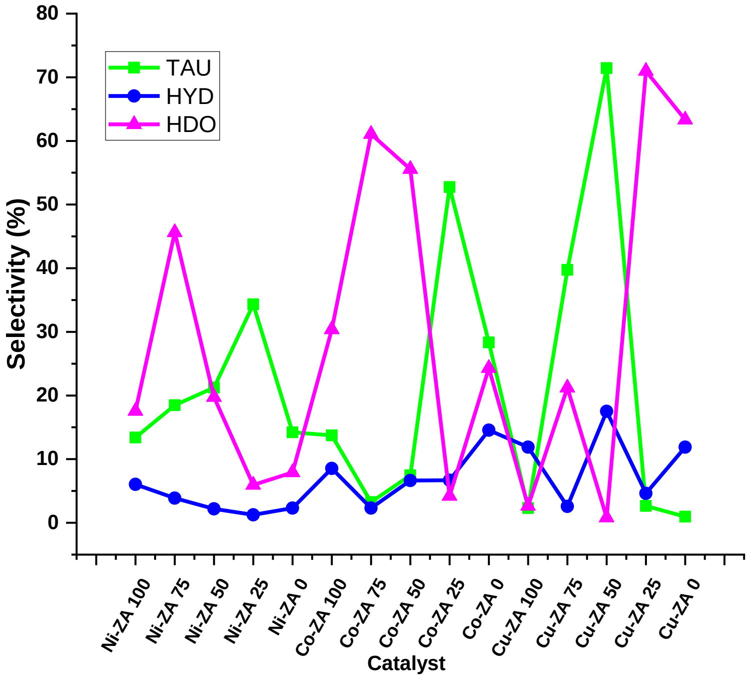


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Figure 5. 14: Trends of product selectivity of Hydrogenation, hydrodeoxygenation and tautomerization of the supported metal catalysts.

As seen from Figure 5.14, all the M-ZA 100 catalysts show relatively low selectivity to cyclic saturates (HDO). The selectivity increases when some alumina is included in the catalyst composition. Selectivity peaks for catalysts Ni-ZA 75, Co-ZA 75, Co-ZA 50, Cu-ZA 25 and Cu-ZA 0. The decreasing trend of selectivity to cyclic saturates is Cu-ZA 25 > Cu-ZA 0 > Co-ZA 75 >Co-ZA 50 > Ni-ZA 75 > Ni-ZA 50. The trend shows that the amount of alumina required for peak selectivity to cyclic saturates decreases in roughly the same order, Cu > Co ≥ Ni. Further, it is observed that the selectivity to cyclic saturates peaks in catalysts with lower alumina content than those in which selectivity for aromatics (TAU) peaks in case of the Co and Ni catalysts. Cu catalysts show an opposite trend.

The trends of Co and Ni catalysts can be explained as follows. Surface concentrations of active metals increases with decreasing zirconia in the catalyst which in turn promotes both HDO and TAU, whereas increase in acidity favors TAU alone. TAU requires bifunctional catalysis. Thus HDO selectivity can be expected to peak in catalysts with relatively lower alumina content (lower acidity) than aromatics (TAU).

As regards selectivity to aromatics (TAU), the trend is Cu-ZA 50>Co-ZA 25 >>Ni-ZA 25. Excepting Cu-ZA 50, the remaining two catalysts have relatively lower zirconia content and hence higher acidity than the catalysts which give peak selectivity to cyclic saturates (HDO). Co-ZA 50 and Cu-ZA 100 show low selectivity to aromatics. This correlates with their low acidity (Figure 5.1). Specific combination of metal and acidity is important as evident from the trends. The Cu catalysts show an opposite trend. Cu-ZA 50 shows peak selectivity for aromatics whereas Cu-ZA 25 shows peak selectivity for cyclic saturates (HDO). Both have similar strong acidity 0.150 and 0.156 mmol NH_3/g catalyst. Hence, reason for this trend is not clear.

As regards oxygenates (which form by HYD) the trend is Cu-ZA 50 > Cu-ZA 0 ~ Co-ZA 0. Ni catalysts show low selectivity to oxygenates (HYD) and there is a slight decreasing trend with decreasing zirconia content. Co catalysts show a slight increasing trend with decreasing zirconia content. The Cu and Co catalysts show relatively better selectivity to HYD products than the Ni catalysts. Literature reports show that cyclic oxygenates are favored at lower reaction temperatures 200-250°C and high pressure 150-200 bar. The current work was carried out at high temperature 350°C and relatively low pressure 10 bar g. This could be responsible for the low selectivity.

5.4.3 Product Yields

Trend of product yields of the three major components, cyclic saturates (HDO), aromatics (TAU) and cyclic oxygenates (HYD) are shown in Figure 5.15 below.

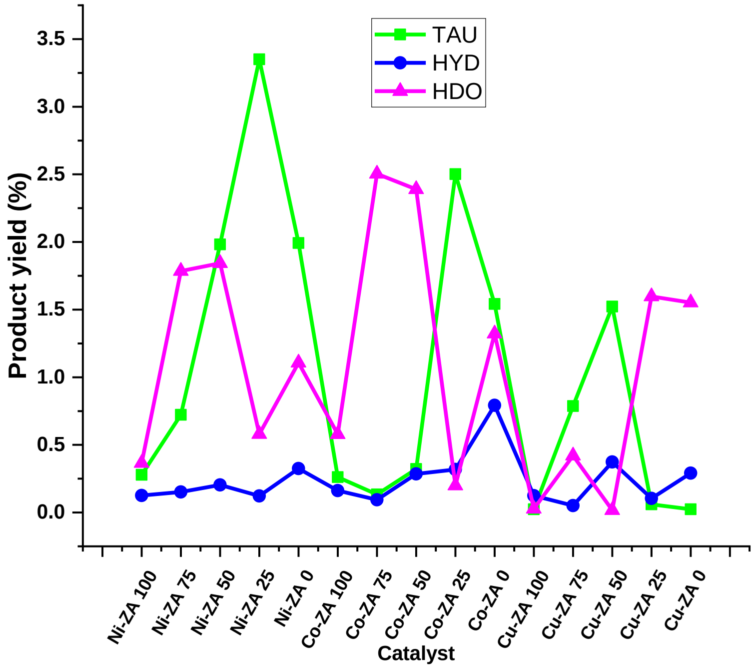

Figure 5. 15: Trends of product yields of Hydrogenation (HYD), hydrodeoxygenation (HDO) and deoxygenation (TAU) of the supported metal catalysts

As seen from Figure 5.15, yields for saturates (HDO) peak at M-ZA 75 – M-ZA 50 for Ni and Co catalysts. This trend is consistent with expectation because HDO is metal catalyzed. Acidity increases with decreasing zirconia content. The increasing acidity favors TAU which is a competing reaction, thus resulting in a decrease in HDO. Trend for yield of cyclic saturates is Co-ZA 75 > Ni-ZA 50 > Cu-ZA 25. Like the Co catalysts, Ni-ZA 50 closely followed by Ni-ZA 75 show highest yields amongst Ni catalysts. This is consistent with requirement of metal function with relatively low acidity for this reaction.

Cu catalysts show a different trend. Cu-ZA 25 and Cu-ZA 0 in that order show better yields for saturates within Cu catalysts, but yield is lower than that of Co catalysts and comparable with that of Ni catalysts.

All the M-ZA 100 catalysts irrespective of active metal show low yield for all three reactions, HDO, TAU and HYD. The reason is attributed to the low surface concentration of active metals (XPS) in these catalysts (Figure 5.4) accompanied by the low acidity (Figure 5.1). Thus both acid and metal catalyzed reactions are affected, resulting in low conversion of m-cresol.

As regards aromatics, the trend of product yield is Ni-ZA 25 > Co-ZA 25 > Cu-ZA 50. The higher conversion of Ni followed by Co is responsible for the change in trend with respect to product selectivity (which was Cu-ZA 50 > Co-ZA 25 >Ni-ZA 25). Thus it is reiterated that certain combinations of metal function and acidity are important for TAU. This is consistent with requirement of bifunctionality for this reaction (TAU).

As regards oxygenates, Co-ZA 0 shows the highest yield followed by Cu-ZA 50. Ni catalysts show low yield to oxygenates. The trends are not consistent with requirement of only metal function for this reaction. As mentioned above the high reaction temperature (350°C) and low pressure (10 bar g), which are not suitable for this reaction, appear to be responsible for low yields to cyclic oxygenates.

Based on the above trends a scheme is proposed for the HDO of m-cresol in Figure 5.16. The scheme is based on the trends of product selectivity realized in the current study. As already mentioned earlier DDO (direct cleavage of C_{ar}-O(H) bond) is energetically not favorable, hence discounted. Disproportionation was a dominant reaction. Lewis acidity from metal oxides appears to be important for this reaction. HDO is observed in catalysts with relatively lower acidity (low alumina content). Increasing acidity further favours the TAU route which forms aromatics. Formation of phenol by demethylation of toluene in alumina rich Ni catalysts is supported by attendant formation of methane (Figure 5.8).

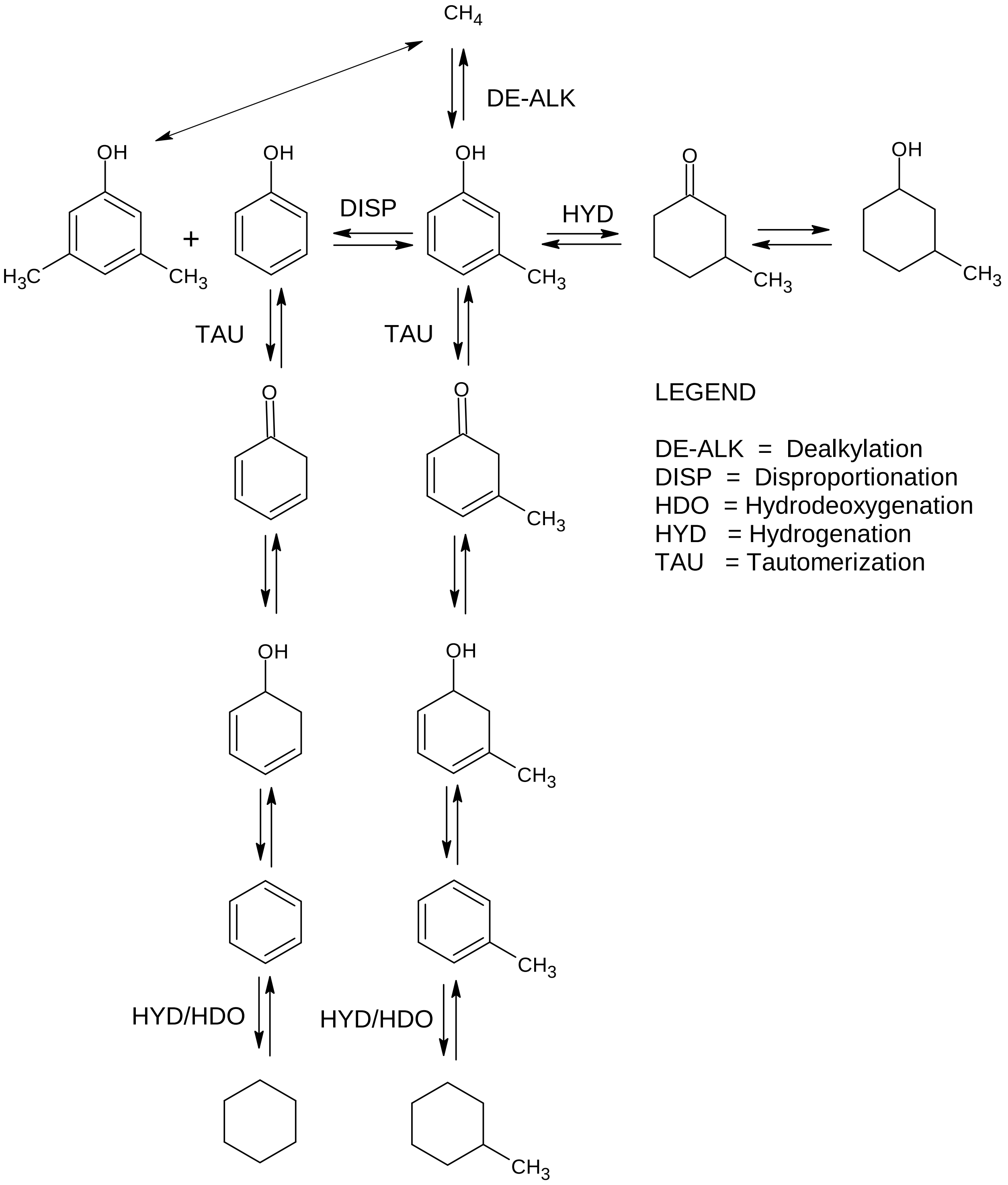

Figure 5. 16: Proposed scheme for HDO of m-cresol

Products of tautomerization follow the trend of increased acidity required for bifunctional catalysis. Cyclic saturates peak on catalysts with relatively lower acidity than those on which aromatics products peak as is expected. Formation of cyclic oxygenates is not favored under the reactions conditions of this study.

The carbon/coke content (wt%) of the spent catalysts from HDO of m-cresol is presented in Figure 5.17 below.

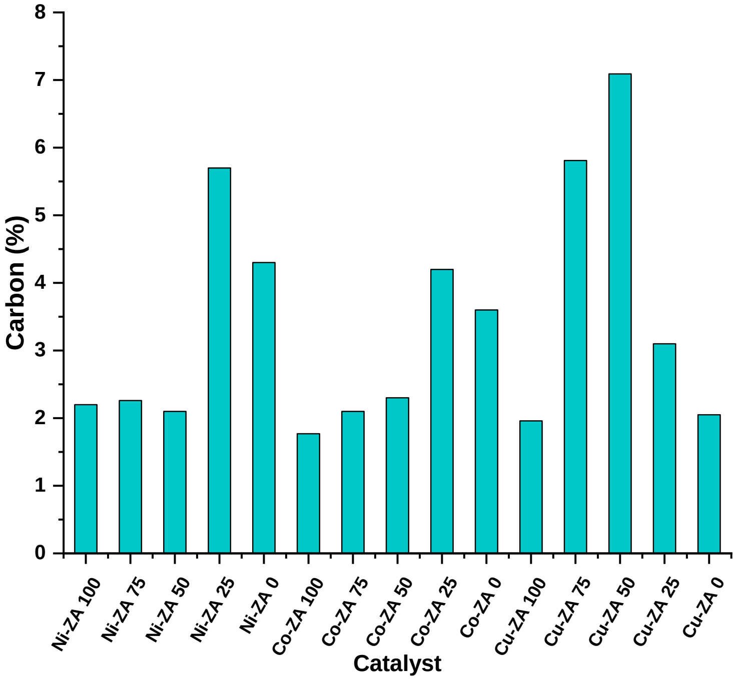

Figure 5. 17: Carbon/coke content of used catalysts after HDO of m-cresol

As seen from Figure 5.17, catalysts Co-ZA 25, Ni-ZA 25, Ni-ZA 0, Cu-ZA 75 and Cu-ZA 50 show significantly more coke than the remaining catalysts. Comparing the trends of coke content of the spent catalyst with those of selectivity for TAU in Figure 5.14, it is clear that catalysts which present a higher selectivity for TAU (aromatics formation) form more coke. The TAU reaction is bifunctional. It requires both acid and metal function. The C/H molar ratio ranged from 0.31 to 0.77 with an average of 0.584 which is characteristic of olefinic coke.

5.5 Conclusions

Hydrodeoxygenation of m-cresol is studied on bifunctional Ni, Co and Cu supported on zirconia-alumina catalysts with varying zirconia:alumina.

XRD crystallite size of the active metal precursors in calcined catalysts and active metals in reduced catalysts correlate well with Metal Support Interaction as determined from TPR. The behavior is consistent with theory based on Tamman and Huttig temperatures. MSI shows dependence on zirconia content of carrier. Thus, Metal support interaction deduced from TPR studies helped correlate differences in metal crystallite size of the active metals with thermal processing steps such as calcination and reduction of catalyst.

Both acid and metal catalyzed reactions occur during deoxygenation. Specific combination of acidity (acid function) and active metal (metal function) are observed to be critical for product selectivity. Especially for Co and Cu catalysts.

Conversion trends well with XRD crystallite size and acidity. Conversion increases with increasing alumina content of catalyst, with the trend Ni>Co>Cu, which correlates with their XRD crystallite size. Catalysts supported on neat zirconia show poor activity which is consistent with larger metal crystallite size, low concentration of active metals on the surface of the catalyst (XPS) and low acidity.

Low surface concentration of Co, Ni and Cu catalysts supported on neat zirconia correlates with their poor activity for all three routes (HYD, HDO and TAU).

Product selectivity depends on specific combination of acidity and metal functionality. Correlation with oxophilicity of active metals is unclear. Phenol, xylenol, cyclohexane, benzene and toluene are main products depending on the acid and metal function of individual catalysts.

Phenol and xylenol form from disproportionation, which is an acid catalyzed reaction. Additional phenol is observed to form in Nickel catalysts with low zirconia content. This appears to form by hydrogenolysis of methyl group of m-cresol. This is supported by attendant formation of CH_4.

Product selectivity's to cyclic saturates by hydrodeoxygenation (HDO route) and to aromatic products by deoxygenation (TAU route) correlate with the metal and acid functions of the catalysts. Lower acidity favors HDO whereas relatively higher acidity favors TAU. Low selectivity to HYD (cyclic oxygenates) is due to the choice of reaction conditions under which the study was carried out. Certain specific combination of active metal and acidity of support were found to be important for product selectivity.

Lewis acidity of the catalyst influences disproportionation of m-cresol to phenol and xylenol and also the formation of benzene and toluene (BTX) by TAU route which occurs either by partial hydrogenation or tautomerization of m-cresol followed by dehydration as a culminating step. This results in formation of aromatics. This is a bifunctional mechanism and requires both acidity and metal function.

Role of metal function is evident from formation of cycloalkanes (saturates), and cyclic oxygenates. Cyclic saturates appear to form by further hydrogenation of cyclic oxygenates.

Thus, the trends in activity and product selectivity were correlated with characteristics of the catalysts such as metal crystallite size and surface concentrations of metals and acidity and also oxophilicity (to an extent).

The results indicate that a small window of combination of metal function and acid function exists in case of Co and Cu catalysts for selectivity to important products such as aromatics and saturates.

Copper catalysts show trends of product selectivity which differ from those of Co and Ni catalysts. This may be due to differences in behavior of its metal support interactions, crystallite size as a function of zirconia content and differences in electronic configuration relative to Co and Ni.

Catalysts which were active for TAU showed more coke formation. The coke was olefinic in nature.

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5.6 References

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