

## Activity Study of Customized Cu Based Catalytic Matrixes with ZnO and/or ZrO<sub>2</sub> Intended for the Enhancement of Active Lifetime and Methanol Yield in Lurgi Process

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**Abstract:** A series of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Cu/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared for methanol synthesis study in Lurgi process. Apart from Cu and Al<sub>2</sub>O<sub>3</sub>, these catalysts would contain ZnO and/or ZrO<sub>2</sub> as active CO hydrogenation sites. The preparation method was an alternative acid-alkali pH precipitation. The SEM-EDX data for the formulations with various atomic ratios showed high homogeneity, hence good intermixing of ingredients. TPR analysis was done on all prepared matrixes and industrial catalyst and showed the reduction temperature of 300 °C to 345 °C for all 3 types of catalysts prepared. Both Low and High Temperature peak obtained for Metal Surface Area (MSA) analysis showed that there is a general decreasing H<sub>2</sub> adsorption trend with the increasing amount of Zirconia in the catalyst. Prepared catalyst sample A with no zirconia present showed highest low and High Temperature adsorption in comparison with commercial and prepared catalysts. This suggests that Cu-ZnO catalyst have higher activity as compared to Cu-Zirconia based catalysts. CO conversion study reveals that sample A with no Zr present has highest conversion of up to 4%. Also determined was that Zn offers higher activity in CO hydrogenation process in catalyst samples compared to Zr when present in the same atomic %. Also monoclinic Zr phase formed in catalyst type Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> gives higher MeOH Yield compared to catalyst sample where tetragonal Zr phase is formed.

**Key words:** Methanol · s-TPR · TPR · XRD · TGA

### INTRODUCTION

The need for environmentally clean and economic viable fuel is a major industrial concern today. Methanol is regarded as one of prime clean energy source and has subsequently become one of the most produced chemical today. As such, the methanol synthesis process and catalyst improvement have become a major agenda in the industrial gas chemistry. The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst which dominates the market suffers from major disadvantages. The limited conversion of up to 0.8% per pass has been for long an issue of academic challenge. Steady and comparatively quick deactivation of this catalyst in industrial reactors had being commonly observed. The deterioration of its mechanical strength (cracks, crumbing/powdering) was reported as well. Currently available commercial catalysts have an active period of 4 years whereby their activity dwindles even in the first year of operation [1]. Current trend in petrochemistry also calls for more advanced catalysts that can be operated without fast aging at more severe conditions. All above said factors stimulated the search

for improvements. The list of changes aimed at an upgrading the matrix of heterogeneous catalyst has been headed by advance methods of preparation of conventional catalysts. The most common method which is co-precipitation is quickly being dismissed as the product catalyst usually shows low tolerance to poisoning, low thermal stability and low activity period [2-3]. Newer methods such as alternative pH precipitation have guaranteed better results and are employed in this study. Also, ZrO<sub>2</sub> has become a new industrial crave as Cu/ZrO<sub>2</sub> and Cu/ZnO/ZrO<sub>2</sub> catalyst have been reported to have high activities, selectivity and stabilities relative to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> [4]. This is explained by the greater Bronstead acid sites on ZrO<sub>2</sub> where methanol is produced by hydrogenation of formate and methoxy species [5]. Therefore the need to study the activity and properties of the combined Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst has been undertaken in this project in comparison with the other catalysts in order to obtain an optimum blend of metals and supports which would have the highest activity and selectivity of methanol. The activity of this catalyst blend would also be compared to the conventional commercial

Table 1: Calculated and SEM-EDX resultant compositions and metal ratios of prepared catalyst and industrial catalyst

Sample	Atomic Composition (%)				Atomic Ratio				peak T, TPR (°C)	H2 ads, μmol
	Cu	Zn	Al	Zr	Calculated		SEM-EDX			
					Zn/Cu	Zr/Cu	Zn/Cu	Zr/Cu		
Ind <sup>b</sup>	52.66	34.37	12.98	0	-	-	0.65	0	325	3586.24
A	42.86	47.62	9.52	0	1.11	0	1.21	0	315	5366.32
B	42.06	46.73	9.35	1.87	1.11	0.04	1.25	0	315	4481.13
C	40.91	45.45	9.09	4.55	1.11	0.11	1.1	0.14	300	4357.60
D	39.82	44.25	8.85	7.08	1.11	0.18	1.23	0.14	310	3880.78
E	40.91	36.36	9.09	13.64	0.89	0.33	1	0.23	320	4037.15
F	42.86	0	9.52	47.62	0	1.11	0	0.47	345	2329.79

<sup>1</sup>Composition of Fresh and Spent Industrial Catalyst from SEM-EDX analysis.

catalyst obtained. The next step of understanding the kinetics and surface reaction of methanol synthesis reaction is necessary to improve catalyst active period. The current Operating Pressure at 50 -100 atm is too high and contributes to sintering of catalysts. The need to improve this by operating at lower Pressure presumably below 30 atm is desirable. The surface conditions also need to be studied further to compliment the current bi-metal of Cu and Zn/Zr alloy active sites theory.

## Experimental

**Preparation of Catalyst Samples:** A series of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Cu/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared. Apart from Cu and Al<sub>2</sub>O<sub>3</sub>, these catalysts would either contain ZnO and/or ZrO<sub>2</sub> as a final mixture. The reactants used are copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), Zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Aluminium Nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), Zirconium nitrate (Zr(NO<sub>3</sub>)<sub>4</sub>·xH<sub>2</sub>O) and Na<sub>2</sub>CO<sub>3</sub>. The method of preparation is a novel Acid Alkali Alternating pH developed recently [6]. Acid site solution consisting of Copper nitrate, Zinc nitrate, Aluminium Nitrate and Zirconium nitrate were mixed accordingly to obtain the catalytic composition as shown in Table 1. The base solution was sodium carbonate. Acid and base solutions were mixed into the mother solution alternatively to reach a desired low and high pH. The acid site pH was 4.88 and base site pH was 8.8. The mother solution was continuously stirred and Temperature was maintained at 70°C. The process was repeated until all acid solution was used and the final pH of mother solution was maintained at 7.1. The solution was aged at 80°C for 2 h under continuous stirring at fixed rpm and then filtered. The filtrate was dried at 110 °C for 12 h. Consequently, it was pressed and grounded to mesh size 60–80 and then calcined at 370°C for 9 h. Commercial catalyst sample was obtained for comparative analyses.

**SPhysical and Chemical Characterization:** Temperature Programmed Reduction (TPR) is conducted for Hydrogen adsorption in order to determine catalyst reducibility and the peak Temperature at which catalyst is reduced. Energy Dispersive Spectrometry probe (EDX) in the SEM was employed to determine the wide area composition of elements on the catalyst surface. This information is particularly useful to determine the Cu/Zn and Cu/Zr ratio on the surface which would verify the compositions of our calcined catalysts without sample destruction. X-Ray Diffraction (XRD) analysis was done at interval 2°/min to determine the various compound phases formed in the catalyst. Thermal Gravimetric (TGA) analysis showed thermal stability of all catalysts. s-TPR analysis was conducted to determine the Low and High Temperature peak adsorption. From this the active Cu metal dispersion, D<sub>Cu%</sub> could be calculated.

**Reaction Conditions:** Catalyst activity was studied in a Micro Tubular Reactor connected to an online Gas Chromatograph (GC 6890-Hewlett Packard) for analysis of product gases. 1g of catalyst sample in between quartz wool layers was loaded into the reactor. Catalyst samples were initially reduced in 5%H<sub>2</sub>/N<sub>2</sub> from room Temperature to samples' peak reduction Temperatures as shown in Table 1. Pure N<sub>2</sub> gas was flown over the sample for 1hr before switching to 30%CO/70%H<sub>2</sub> reaction gas mixture with the WHSV (Weight Hourly Space Velocity) of 2982 hr<sup>-1</sup>. Reaction was maintained for 3.5 hours as by then reaction had achieved stability.

## RESULTS AND DISCUSSION

Table 1 shows the atomic composition of all the prepared catalysts (A, B, C, D, E, and F) as well as commercial catalyst (Ind). There is no Zr metal present in

catalyst A and Ind. These two catalysts are part of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> series. The Zr composition steadily increases from catalyst A to E. These are a series of Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Catalyst F alone is a Cu/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The atomic composition of Cu and Al<sub>2</sub>O<sub>3</sub> was maintained almost constant in all prepared catalysts so that only ZrO<sub>2</sub> and ZnO compositions would be the observed variables. This however was not the case for commercial catalyst, Ind as its composition is already fixed. The calculated Zr/Cu and Zn/Cu ratio is compared with the EDX resultant ratios in Table 1.

**Temperature Programmed Reduction:** As can be seen in Table 1, the catalyst reduction temperature was found to be optimum at around 300 - 345°C for all catalysts. This shows that metal composition of the catalyst formulation would not affect the characteristic reduction temperature. As shown in Table 1, Sample A has the highest amount of H<sub>2</sub> adsorbed among all samples including the commercial catalyst, Ind. The H<sub>2</sub> adsorption is represented by the Area under the curves shown in Figure 1. There is a general decreasing trend of H<sub>2</sub> adsorption as the amount of Zr in the sample increases from sample A to F. This would suggest that Zr has a negative effect on Cu activity.

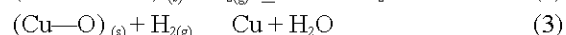
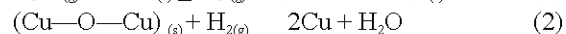
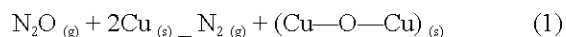
**X-Ray Diffraction:** XRD patterns are shown in Figure 2 for all the samples prepared as well as for used and fresh industrial catalysts. The sharp pattern would represent clearer crystal formation while the diffused pattern represents good mixing of elements. Industrial fresh catalyst has the best mixing while the spent Industrial catalyst has the lowest. All prepared catalysts show similar peak sharpness suggesting little influence of compositions or metal types on elemental mixing. The characteristic peak for CuO is at Bragg's angle 35.44° and 38.66°. For  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the peak is at 32° and for ZnO it's at 34.33°. In samples A to F, the Zr metal addition caused the formation of Zirconia crystal which has a characteristic peak at 25° as well as 28.5°, 48°, 57° and 67°. The increase in peak height from catalysts A to F at Bragg's angle 28.5° is due to the increase in Zirconia phase composition as shown in Table 1.

**Thermal Decomposition Study:** Thermal gravimetric method (TGA) was conducted on dried and calcined catalyst sample C to study the effectiveness of calcination to remove salts. The graph of catalyst weight change (%)

vs. Temperature was plotted. From Figure 3, it can be seen that thermal decomposition of metals nitrates into metal oxides in dried catalyst sample occurs at Temperatures below 350 °C. At this temperature, the weight change of catalyst is the graph is at minimum and hence catalyst sample is completely oxidized. Thus this shows that calcination Temperature at 350°C is suitable for removal of salt nitrates.

The peak Temperature where decomposition occur the most is at the range of 30–130°C and 170–280°C. This range is somewhat consistent with the boiling point Temperature for copper nitrates which is at 170°C, for zinc nitrate at 105°C, for Aluminium nitrate at 134 °C and finally zirconium nitrate at 100°C under atmospheric pressure [7]. This indicates all other metal nitrates are oxidized at the lower Temperature range while copper nitrate is oxidized at the upper Temperature range.

**Metal Surface Area Calculation (MSA):** Cu has a distinct surface and bulk copper active sites. Through N<sub>2</sub>O adsorption (1) and subsequent H<sub>2</sub> s-TPR [8], the surface active sites were distinguished as Low Temperature H<sub>2</sub> adsorption peaks (2) and bulk active sites as High Temperature H<sub>2</sub> adsorption (3) peaks. The surface copper sites, Cu<sub>2</sub>O are the main active sites in the Lurgi process as they adsorb H<sub>2</sub> at low Temperatures around 150–200 °C as shown in Figure 4. The High Temperature peaks represent almost inert oxidized Cu sites at they are present in CuO form and are only reduced at Temperatures above 400°C which is way above the Lurgi operating Temperature of 250°C. Therefore, greater the Area under the curve of Low Temperature peaks are an indication of larger availability of active Cu sites and thus greater activity.



As can be seen from the signals in Figure 5, there is a general decreasing trend of H<sub>2</sub> adsorption for catalyst samples as Zr amount in catalyst increases at both High and Low Temperatures. Prepared sample A has the highest Low and High Temperature peak among all the prepared catalysts. Industrial catalyst however still has higher Low temperature peak but very low High Temperature peak. This would suggest highest activity of catalyst A among prepared samples.

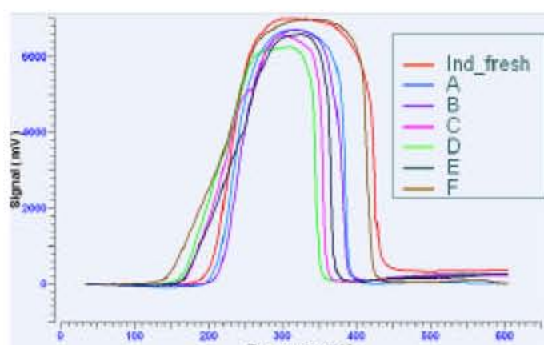


Fig. 1: TPR results of samples showing temperature at which catalyst reduction took place. Samples are labeled on right side of graph

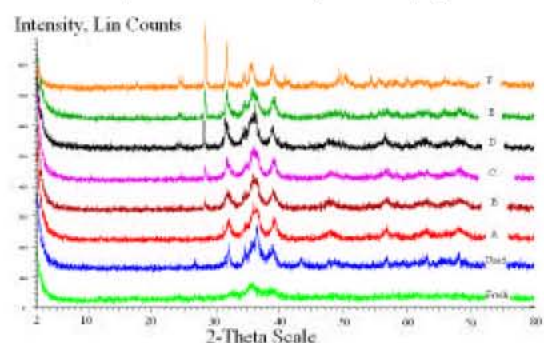


Fig. 2: XRD results showing compound peaks of all samples. Samples are labeled on right side of graph

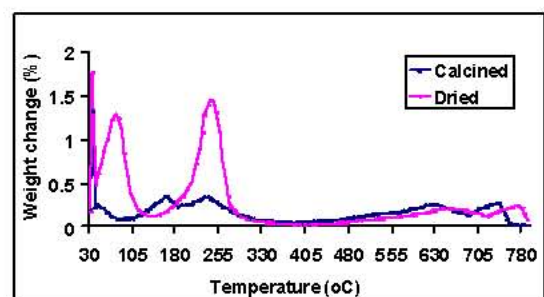


Fig. 3: TGA graph of catalyst weight change (%) vs. Temperature for Dried and Calcined catalyst Sample C.

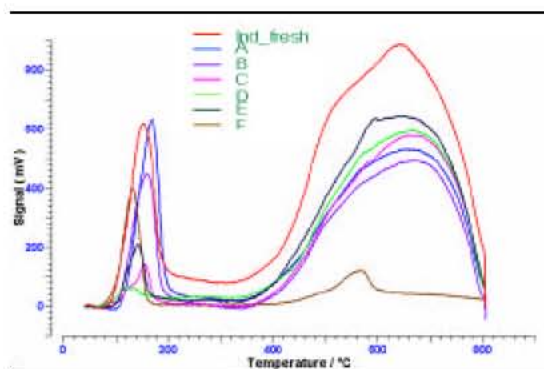


Fig. 4: s-TPR spectrum of catalysts after  $N_2O$  adsorption.

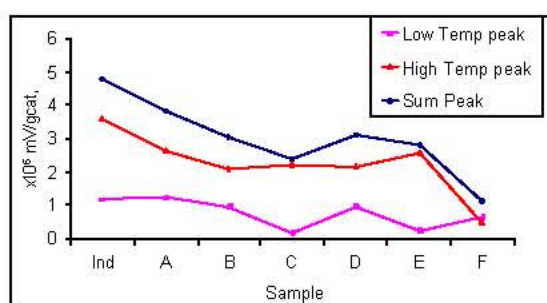


Fig. 5: Signals showing the Low Temperature, High Temperature and their sum after the s-TPR for catalyst samples

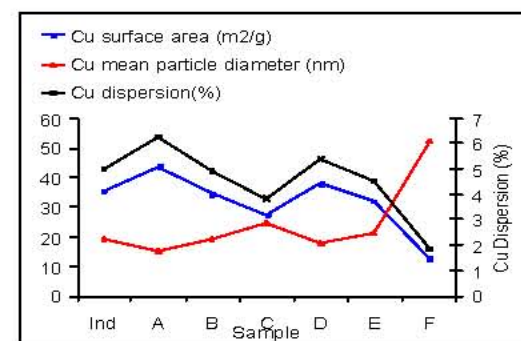


Fig. 6: Metal surface Area (MSA), Cu mean particle diameter ( $D_p$ ), and Cu dispersion ( $D_{Cu}$ ) on catalyst surface for all prepared and commercial catalysts samples

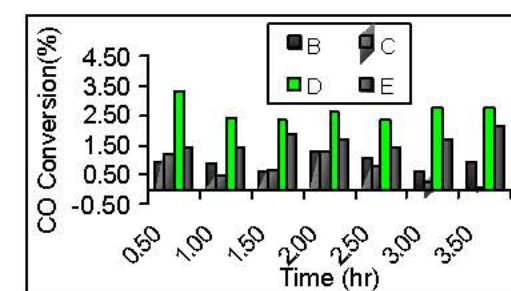


Fig. 7: CO conversions in % for all Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type catalysts sample B, C, D and E.

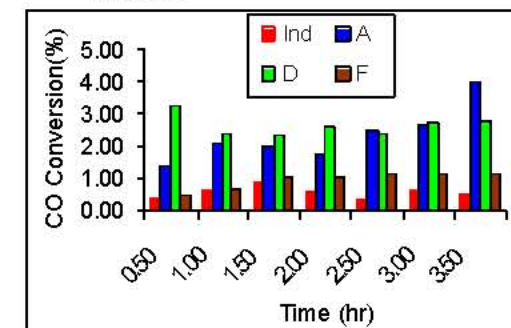


Fig. 8: CO conversions in % for commercial catalyst samples Ind and prepared catalyst samples A, D and F.

From the given formulas [8], the Metal surface Area (MSA), Cu mean particle diameter ( $\bar{d}_{av}$ ), and Cu dispersion ( $D_{Cu}$ ) have been calculated and are shown for all catalyst samples in Figure 6. As can be seen there is a generally decreasing trend of MSA and  $D_{Cu}$  as the amount of Zr in the catalyst increases. This is starkly consistent with all the other findings we have had thus far. Also shown in Figure 5 is the increasing Cu particle diameter as the amount of Zr in the catalyst increases. Large particle diameters are generally linked to sintering and thus catalyst lower surface activity. Catalyst sample A has the highest Cu surface area and dispersion suggesting greater activity than the commercial catalyst, Ind.

**Activity Study:** Two key properties are used as gauges for comparison of catalyst activity for all catalyst samples with variant metal compositions as displayed in Table 1. They are CO Conversion ( $X_{CO}$ ) and Selectivity of MeOH ( $S_{MeOH}$ ).

$$X_{CO} = \frac{(n_{CO})^i - (n_{CO})^f}{(n_{CO})^i \times g_{cat}} \times 100\%$$

$$S_{MeOH} = \frac{(n_{MeOH})^f}{\sum (n_x)^f} \times 100\%$$

**Analysis of CO Conversion:** It can be clearly seen from Figure 7 that the highest CO conversion among Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples is obtained for Sample D. Although the conversion rate changes throughout the period of study, it is still within the range of 2.5 to 3.5%. Sample B and C have extremely low CO conversion rates of 0.2 to 1.2 %. The conversion rate of Sample is lower than Sample D but higher than Sample B and C at around 1.25 to 2.0%.

This conjures a very interesting point in the picture regarding the role of Zn and Zr in catalyst activity. It explores a unique combination of both Zn and Zr in the process of achieving maximum activity. Sample B and C have low Zr amount although high Zn but with low activity. Sample E however, has high Zr/Cu ratio of 0.33% but lower Zn/Cu ratio at 0.89%. Sample D has higher Zn/Cu ratio of 1.1% compared to sample E but with lower Zr/Cu ratio of 0.18%. Since Sample D has higher activity than Sample E, it shows that Zn has precedence over Zr in order of importance of metals that increase catalyst activity, i.e. facilitate the CO hydrogenation process on its surface.

Figure 8 on the other hand, shows the CO conversion at 30 minutes interval over a period of 3.5 hours of 3 different catalyst type representatives and Commercial catalyst as control, i.e. Commercial sample, Ind of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> type, Sample A of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> type, Sample D of Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type and Sample F of Cu/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type.

From Figure 8 it can be seen that Sample A has the highest CO conversion up to 4% followed closely by Sample D up to 3.5%. Commercial Sample, Ind has very low CO conversion in the range of 0.3 to 0.75 % and Sample F which has no Zn in it has low activity as well in the range of 0.5 to 1.0%. For commercial sample Ind, its low activity is justified as it has very low Zn/Cu ratio of 0.65 as shown by the EDX study in Table 1. This low amount of Zn would most definitely limit the CO hydrogenation capacity of the catalyst.

Sample F contains a Zr/Cu ratio of 1.11 in contrast to Sample A which contains a Cu/Zn ratio of 1.11. However the low activity of Sample F and the very high activity of Sample A indicate strongly the previously stated notion of Zn being able to hydrogenate CO more effectively than Zr and hence increase metal activity.

Sample D and A however show a unique set of CO conversion rates over a period of 3.5 hours study. For the first 2 hours the CO conversion of Sample D is much higher than Sample A, but after that, the CO conversion of Sample A increased especially towards the last ½ hour of the study. This could be due to the effect of hysteresis in Sample D which is not so obvious in Sample A. Hysteresis happens when after a period of adsorptions of gas on catalyst surface and the formation of multilayer of adsorbed molecules on the catalyst surface occurs. This hinders the motion of the desorbed product gas away from the surface of the catalyst and thus impedes the reaction rate. This effect apparently as can be inferred from Figure 8 is more common on Zr surface than it is on Zn surface. This is because as the rate conversion of CO on catalyst Sample A increases steadily, the rate of conversion on the catalyst Sample D decreases until it reaches steady state.

The conversion rate per pass of CO in a methanol synthesis process has been reported to be around 0.8% for industrial type Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts at Pressure 50 bar and Temperature 224°C [9]. This is consistent with the obtained CO conversion in the range of 0.35%-0.84% for the commercially obtained catalyst sample,



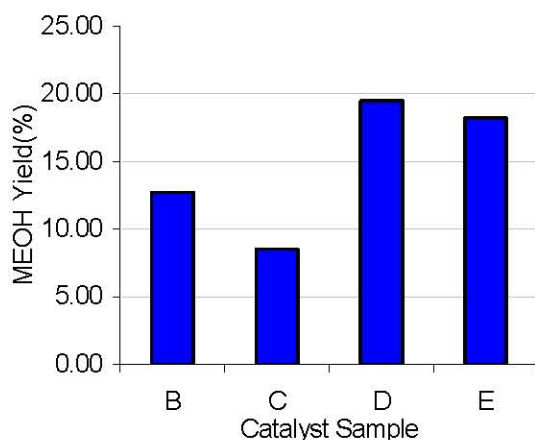


Fig. 9: Steady state MeOH Yield in % for all Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type catalysts sample B, C, D and E

Ind in our study as shown in Figure 8. This fact points out the low conversion rate per pass on current industrial scale and the potential of the prepared sample A and D to improve the methanol synthesis process.

**Analysis of MeOH Yield:** Methanol selectivity,  $S_{MeOH}$  was defined as concentration in mol% of methanol in the product gas over total concentration of all other products  $\sum(n_i)^{\%}$  in the product gas.

Figure 9 shows the steady state MeOH Yield comparison between 4 catalyst samples (B, C, D, and E) of type Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with variant composition of Zr and Zn at hour 3.5 of reaction study. At this point, methanol yields by all catalyst samples have somewhat stabilized. It can be seen clearly that the highest MeOH yield among this catalyst type is given by catalyst sample D followed closely by sample E and finally by sample B and C. This trend of MeOH yield is exactly the same as CO conversion given in Figure 7. This enforces the prior notion in Section 3.6.1 that the catalyst activity is strongly dependent on both Zn and Zr composition but that Zn composition has precedence over Zr in order of importance of metals that increase catalyst activity, i.e. facilitate the CO hydrogenation process on its surface.

The MeOH yield in Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type catalyst samples can also be affected to the phase of metal Zr formed in them. As can be seen in Table 1, Sample D has formed the Zr of monoclinic type while sample B, C and E have formed tetragonal Zirconia. It has been reported that the CO and CO<sub>2</sub> adsorption capacity in monoclinic zirconia is greater leading to an activity 5 times greater than in other forms of zirconia [10]. This explains the high

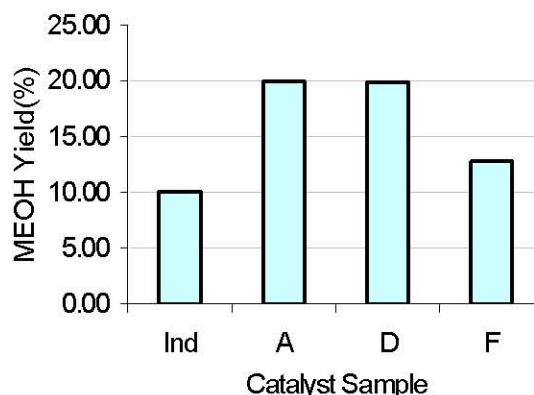


Fig. 10: Steady state MeOH Yield in % for commercial catalyst samples Ind and prepared catalyst samples A, D and F

MeOH yield in Sample D and lower in other Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst types.

Figure 10 however, shows the steady state MeOH Yield at hour 3.5 for 3 different catalyst type representatives and Commercial catalyst as control, i.e. Commercial sample, Ind of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> type, Sample A of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> type, Sample D of Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type and Sample F of Cu/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> type. MeOH yield by given by catalyst sample A and D are much higher up to 20% as compared to a lower yield given by sample F, 12.78% and finally the lowest yield given by commercial catalyst sample, Ind at 10%. This trend too is similar in nature to the CO conversion trend by these samples given in Figure 8.

## CONCLUSION

The characterization of the prepared catalyst of various compositions and support types was done together with the Industrial fresh and used catalyst successfully in this first part of the study. The type of Zirconia compound formed in the catalyst was monoclinic Zirconia which has higher reported activity than the variant tetragonal Zirconia. Also, a range of 300 to 345°C of reduction Temperature was determined. The thermal stability of prepared catalyst was also higher than industrial catalyst at the industrial operating Temperature of 250 °C. Catalyst A also has the highest Low Temperature peak among all prepared catalysts as well as highest dispersion and metal surface area than the industrial catalyst. This is a strong indicator of high activity.

As predicted by s-TPR analysis of Low and High Cu surface area, sample A has the highest CO conversion as well as MeOH selectivity. However this alone was not the gauge for activity as the Zn/Cu and/or Zr/Cu ratio too played a major role. Zn/Cu ratio below 1 reduced catalysts activity as seen in the case of commercial sample, Ind.

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