

Comparison of Gold-Based and Copper-Based Catalysts for the Low Temperature Water Gas Shift Reaction and Methanol Synthesis

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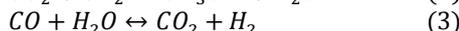
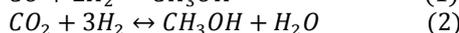
ABSTRACT

The water gas shift reaction was studied over CuO/ZnO/Al₂O₃ (CZA) and 1% Au/CeZrO₄ catalysts and it was found that the gold based catalysts are superior to the copper based catalysts for low temperature WGS. Methanol synthesis was studied over a series of catalysts (CZA, Cu/CeO₂, CuO/MnO/ZnO, 1% Au/CeZrO₄ and 5% Pd/Al₂O₃) at different operating conditions: T=200-260 °C, P=20-50 bar, H₂/CO molar ratio=2/1, GHSV=2640 mlg⁻¹h⁻¹. The catalysts were characterized using BET, in-situ XRD, TPR characterization techniques.

1. INTRODUCTION

Methanol (MeOH) production from synthesis gas has been used successfully for several decades. The low-pressure methanol synthesis replaced the high-pressure methanol synthesis in the 1960s. The low-pressure process was achieved by producing a sulphur-free synthesis gas that enabled imperial chemical industries (ICI) to use the more active Cu/ZnO catalyst. The low-pressure synthesis route operates between 50 and 100 bar.¹ Copper based catalysts have become the main for low-pressure methanol processes. Nowadays, copper-based catalysts are considered the conventional methanol synthesis catalyst. Usually the catalyst contains copper in the oxide phase and zinc oxide and alumina as a support (CuO/ZnO/Al₂O₃), in which the support oxides play minor role in the reaction mechanism.²

The main reactions in methanol synthesis from syngas are the formation of methanol from CO hydrogenation (equation (1)) and CO₂ hydrogenation (equation (2)). The H₂O formed is reacted with CO to form H₂ and CO₂ in the water gas shift reaction (WGS) (equation (3)):



Many researchers have studied the kinetics of methanol synthesis intensively over the copper based catalysts to find which reaction is predominant in methanol formation, CO hydrogenation (equation (1)) or CO₂ hydrogenation (equation (2)). Many researchers indicate that methanol synthesis takes place from CO₂

and not from CO hydrogenation and the CO₂ is the main source of carbon in methanol.³⁻⁵ Skrzypek⁴ et al. found that using a feed of various H₂ and CO ratios with no CO₂. No methanol was formed if steam was completely removed from the feed because small amounts of water were shown to initiate methanol synthesis by the water gas shift reaction and the optimum concentration of CO₂ in (H₂+CO+CO₂) mixture is 1-4%.⁵⁻⁶ As shown from above equations, the WGS (equation (3)) is considered as one of the three main reactions for MeOH synthesis from syngas. Therefore to design a MeOH synthesis catalyst, it is important to optimize its operating conditions that suit the process.

Copper based catalysts are considered to be the standard for methanol synthesis. Various forms such as CuO/ZnO⁷, CuO/ZrO₂⁸, CuO/ZnO/ZrO₂⁹, CuO/ZnO/Al₂O₃¹⁰, CuO/MnO/ZnO¹¹, and CuO/ZnO/Al₂O₃-M (M=Ga-La-Y-Zr)¹² have been developed. Industrially a CuO/ZnO/Al₂O₃ (CZA) catalyst is commonly used as a metallic function for MeOH synthesis reaction.

Also currently, CuO/ZnO/Al₂O₃ (CZA) is used as the standard low temperature shift catalyst, but catalysts based on copper supported on SiO₂, MgO, and Cr₂O₃ also have been applied.¹³ The currently used industrial CZA catalysts for both MeOH and WGS are usually operated at 493–553 K. The reaction at lower temperature leads to the low reaction activity, while higher temperature results in the sintering of the catalysts.

More recently that it has been demonstrated that supported gold catalysts are promising low temperature WGS; Au/ZrO₂¹⁴, Au/TiO₂¹⁵⁻¹⁶, Au/CeO₂¹⁷⁻²¹ and Au/CeZrO₄²²⁻²⁵. Foncesca²³ et al. showed that Au/CeZrO₄ catalysts prepared by deposition-precipitation method have higher activity for the water-gas shift reaction using a model reaction gas mixture than Au supported on CeO₂, TiO₂ or ZrO₂. They studied the stability of Au/CeZrO₄ catalyst both by extended temperature ramps under model WGS conditions and ex-situ steady state ageing with a realistic WGS feed. However, they found that both approaches resulted in deactivation of the catalyst. Pilasombat²⁶ studied the

influence of the preparation method on the catalytic activity of Au/CeZrO₄ catalysts for the WGSR.

The main objectives of this paper are to investigate different catalysts for MeOH synthesis reaction, to compare the catalytic activity of Au/CeZrO₄ catalyst to CZA catalyst for WGSR, to investigate the effect of addition of Au/CeZrO₄ catalyst to CZA catalyst for MeOH production and to investigate the effect of temperature and pressure on CZA catalyst.

2. EXPERIMENTAL

2.1 CATALYST PREPARATION

2.1.1 Material

The chemicals used in the present study were all analytical grades and supplied by Aldrich, UK. These were copper nitrate [Cu(NO₃)₂·2.5H₂O], zinc nitrate [Zn(NO₃)₂·6H₂O], aluminum nitrate [Al(NO₃)₃·9H₂O] and sodium carbonate Na₂CO₃,

2.1.2 CuO/ZnO/Al₂O₃ Catalyst

The CuO/ZnO/Al₂O₃ catalyst was prepared by a conventional co-precipitation method with a wt% ratio of CuO:ZnO:Al₂O₃=6:3:1. The mixed solutions of copper, zinc and aluminum nitrate and an aqueous solution of Na₂CO₃ were added drop wise to a beaker which contained deionized water, under continuous mixing at 70 °C. The pH was adjusted to seven during precipitation by controlling the flow rates of two liquids. After precipitation, the precipitate was aged at the same temperature under continuous stirring. The precipitate was then filtered and washed several times and then the solid obtained was dried and calcined. For simplicity this catalyst is designated and labelled as CZA.

The catalysts used in this study are shown in Table (1).

Table (1): Catalyst labelled in this study.

Catalyst name	Details
CZA	CuO/ZnO/Al ₂ O ₃
PB1CuCe350	10 wt% Cu/CeO ₂ which prepared using by co-precipitation method and calcined at 350 °C for 12 hours
PB2CuCe350	10 wt% Cu/CeO ₂ which prepared using by co-precipitation method at constant pH and calcined at 350 °C for 12 hours
DPCuCe400	10 wt% Cu/CeO ₂ which prepared using deposition precipitation (DP) method and calcined at 400 °C for 2 hours
Gold based catalyst	1% Au/CeZrO ₄ which prepared by DP method.

2.2 CATALYST ACTIVITY for WGSR

Kinetic measurements were carried out in a 6 mm i.d. isothermal quartz tube microreactor placed in ceramic tube furnace controlled by eurotherm2604 controller. The reactor was loaded with 75 milligram of powdered 1% Au/CeZrO₄ catalyst in between two glass wool

plugs in the middle. The bed temperature was measured with K-type thermocouples. The gas flow rates were controlled by mass flow controllers (Aera). The liquid deionized water was delivered using a high performance liquid chromatography pump and then passed through a hot zone at 130 °C in order to generate steam; this steam was then blended with the other gas to create the required mixture with a total flow rate 50 cm³/min.

The catalyst was activated 'in situ' by heating the bed to 90 °C under He with a ramp rate of 1 °C min⁻¹. Then, the WGS mixture was fed to the reactor and samples collected every 25 mins. The temperature was increased continuously until it reached required temperature and then remained at that temperature.⁵

On-line analysis of the reactants and products was performed using a Perkin Elmer Auto System XL ARNEL gas chromatograph equipped with a thermal conductivity detector (TCD). A HayeSep DB column was used (30" x 1/8" SS packed with HayeSep DB 100/120 mesh), which separates CO, H₂, CO₂ and H₂O components. No side reactions were observed during experimental runs. The optimal conditions for the oven to separate these components were: initial temperature, 85°C (5 min); ramp, 15 °C min⁻¹; final temperature, 175°C (10 min). The collection and data analysis were done using TotalChrom software.

2.3 Catalyst Activity for MeOH Synthesis

The reaction was carried out in an isothermal fixed bed reactor made of stainless steel with an inner diameter of 6 mm placed in ceramic tube furnace. The pressure of the reactor was controlled by means of back pressure regulator. The activity tests were carried out in the following conditions: a temperature range from 200 to 260 °C, a pressure from 20 to 50 bar and a space velocity of syngas mixture of 2640 ml.h⁻¹.g⁻¹cat. It was required that the lines after the reactor were heated electrically to temperature greater than the dew point of the outlet gas mixture to avoid condensation. On-line analysis of the reactants and products were measured using Perkin Elmer; Clarus 500 Arnel valved gas chromatograph, equipped with a thermal conductivity detector (TCD) and Auto-Ignite Flame Ionisation.

The equipment setup used in this study is represented in Figure (1). The Methanol and DME synthesis were carried out in an isothermal fixed bed reactor made of stainless steel with an inner diameter of 6 mm placed in ceramic tube furnace controlled by eurotherm2604 controller. Typically 250 mg of the catalyst in the form of pellets (0.25-425 mm) was placed in the centre of silicon carbide (SiC) packing bed (Figure (1)) to keep the temperature uniform through the bed and to prevent the movement of the catalyst because of high pressure. The middle of the catalyst bed temperature was measured with K-type thermocouples. The pressure of the reactor was controlled by means of back pressure regulator and the syngas flow rate was controlled by a mass flow controller (Bronkhorst UK Ltd). Before the reaction the catalyst was activated in situ with (5% H₂/He) at 250 °C for 6 hrs under atmospheric pressure. After that the catalyst was exposed to the

syngas mixture (BOC gases) contained (62% H₂, 31% CO, 4% CO₂ and 3% Ar)⁶. The activity tests were carried out in the following conditions: a temperature range from 200 to 260 °C, a pressure from 20 to 50 bar and a space velocity of syngas mixture of 2640 ml.h⁻¹.g⁻¹.cat. It was required that the lines after the reactor were heated electrically to temperature greater than the dew point of the outlet gas mixture to avoid condensation. On-line analysis of the reactants and products were measured using Perkin Elmer; Clarus 500 Arnel valved gas chromatograph, equipped with a thermal conductivity detector (TCD) and Auto-Ignite Flame Ionisation Detector (FID). A Hayesep D column was used (3m x 1/8" SS packed with Hayesep D 80/120 mesh) for the separation of CO, CO₂, DME, MeOH, CH₄, C₂H₄, C₂H₆, ethanol, propanol, and butanol. The samples were taken every 34 min.

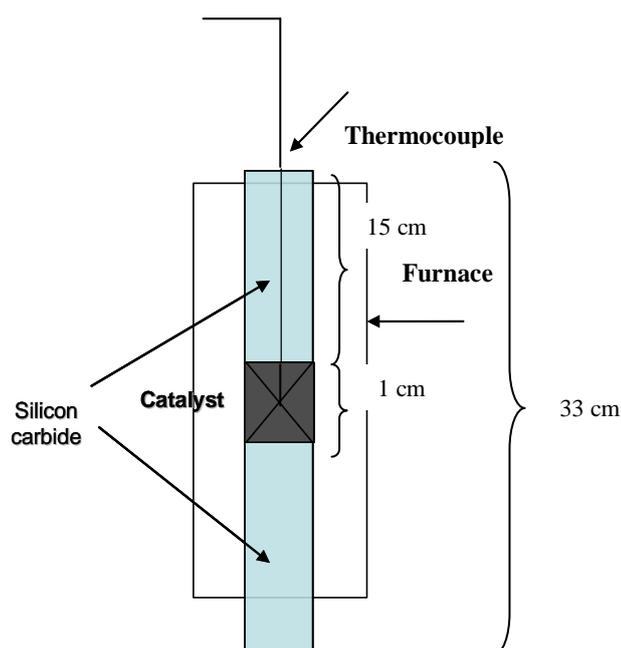


Fig. 1: Micro fixed bed reactor in MeOH and DME Rig

2.4 CATALYST CHARACTERIZATION

XRD technique, BET characterisation, elemental analysis, DRIFTS and Raman Spectroscopy were used.

The reducibility of the catalysts was investigated using TPR technique. All the TPR experiments were performed on a Micromeritics Autochem 2910 apparatus and the H₂ uptake was monitored by a TCD from -50 to 700 °C under flowing 5% H₂/Ar. Before TPR analysis, all the samples were pretreated at 500 °C under flowing 10% O₂/He, and then the temperature was decreased to -50°C under flowing Ar before starting the TPR experiment.

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to determine the actual amount of metals (Cu, Zn, Al and Au) in the calcined catalyst.

3. RESULTS AND DISCUSSION

3.1 Catalytic tests for WGSR

The activity of the gold and copper based catalysts was compared using a full feed (2% CO, 2.5% CO₂, 7.5%

H₂O and 8.1% H₂) and using a feed free from carbon dioxide and water (2% CO and 7.5% H₂O) for WGS reaction. Fig. 2 shows the effect of reaction products (CO₂ and H₂) in the feed on the catalyst activity of Au/CeZrO₄ and CuO/ZnO/Al₂O₃ catalysts at 200 °C. It can be seen that CO conversion is strongly affected by the presence of CO₂ and H₂. For both catalysts, CO conversion is higher in case of feed free from carbon dioxide and hydrogen (only CO and H₂O). It can be seen also that the gold based catalyst is more active than copper based catalyst regardless the feed composition. In the presence of reaction products in the feed (CO₂ and H₂) with CO and H₂O, the CO conversion over copper based catalyst, reaching only 10%, compared with 40% over gold based catalyst.

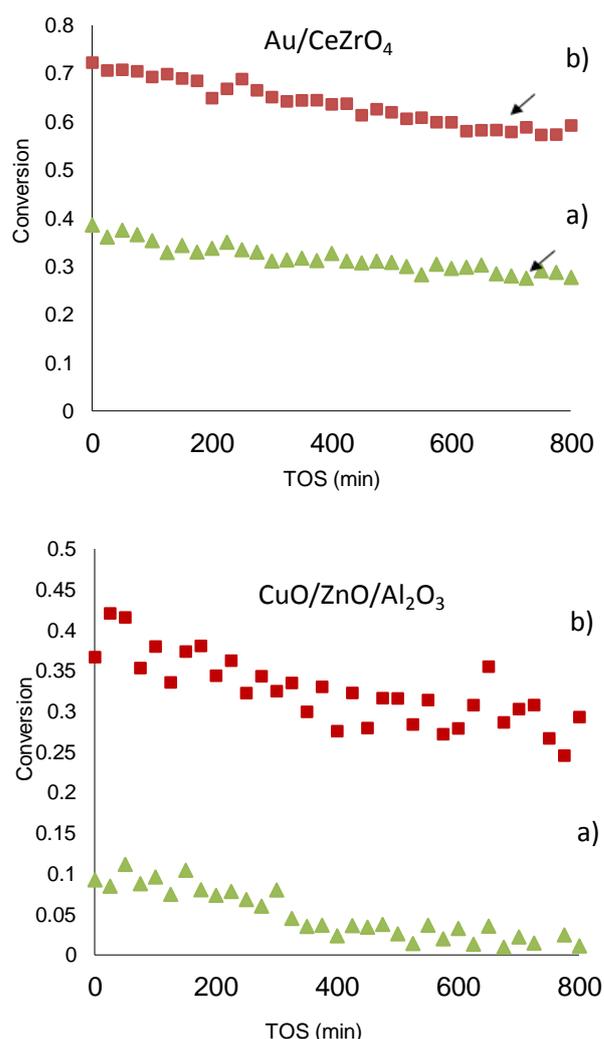


Fig. 2: Effect of reaction products in the feed stream over CO conversion for Au/CeZrO₄ and CuO/ZnO/Al₂O₃ a) full feed (2% CO, 2.5% CO₂, 7.5% H₂O and 8.1% H₂) and b) for feed free from CO₂ and H₂ (2% CO and 7.5% H₂O)

3.2 Catalytic tests for MeOH

The various catalysts prepared by different preparation methods for MeOH synthesis were tested to investigate the activity. The preparation of MeOH synthesis catalysts was explained in section 2.2.3. Figure (3) shows the methanol synthesis for different catalysts

(CuO/ZnO/Al₂O₃, PB1CuCe350, PB2CuCe350, 1% Au/CeZrO₄, 5% Pd/Al₂O₃ and DPCuCe400) at 250 °C and 50 bar, if this figure is zoomed to Fig. 4 to see the conversion of low activity catalysts. It is seen from this figure that all copper based on ceria and Pd/Al₂O₃ catalysts for all preparation methods exhibit very low activity, in which the maximum % MeOH is around 0.45 % for DPCuCe400 catalyst. For gold based catalyst, maximum % MeOH reached is 1.8 % and then decreases very quickly.

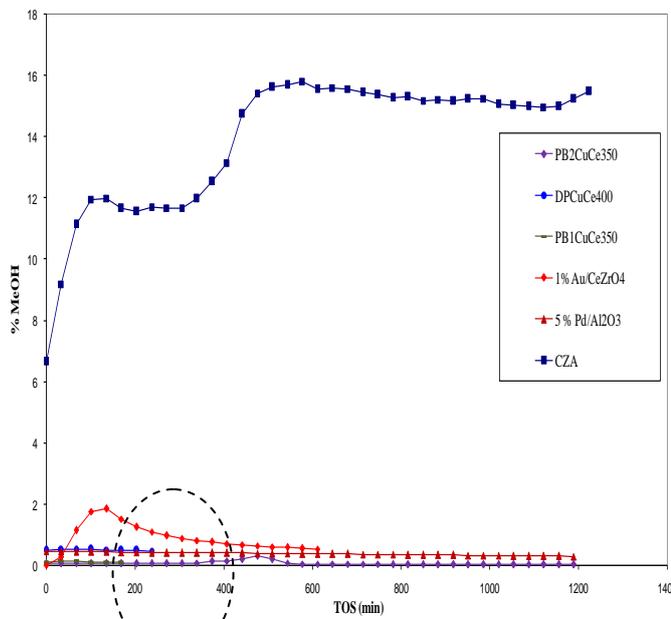


Fig. 3: MeOH % in the product stream using different metal catalyst @ 250 °C and 50 bar

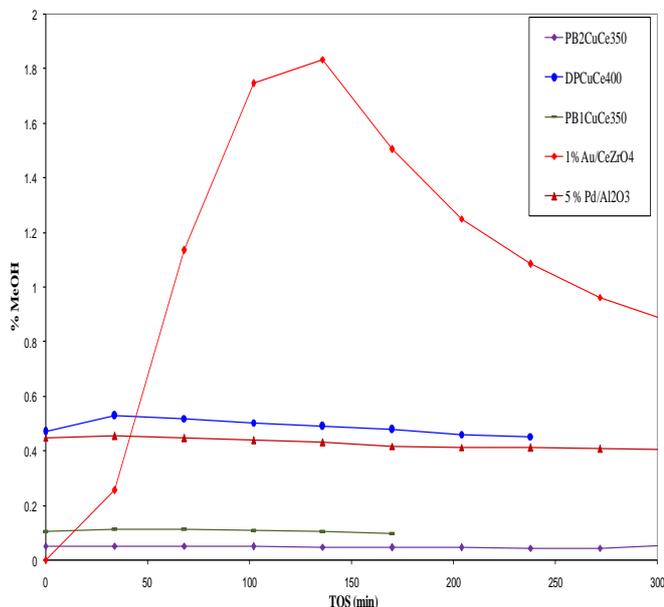


Fig. 4: MeOH % in the product stream using different metal catalyst @ 250 °C and 50 bar

Such a decrease is related to fast deactivation of the catalyst which starts after 150 minutes on stream. As

shown in Fig. 3 the activity of CZA is increased during exposure of the reduced catalyst to the syngas mixture until it reaches to steady state after 200 min. It is clear from Fig. 3 that for CZA catalyst the % MeOH is 12 and then increased to 16, this can be attributed to at the beginning the lines are not heated enough to prevent the condensation of MeOH, when the lines heated to temperature above the dew point this prevent the condensation of MeOH in the lines and increase the concentration of MeOH in the outlet stream to 16 %. Based on the results presented in Fig. 3, it can be concluded that CZA is the best catalyst for methanol synthesis.

3.2.1 Thermal Effect on CZA Catalyst

To study the effect of temperature changes on the stability of CZA catalyst, the catalyst was exposed to reaction conditions at 200 °C and then heated up with rate of 5 °C/min to 250 °C. The temperature was brought back down to 200 °C again as shown in Fig. 5. It is clear that the % MeOH produced is increased with increasing temperature from 200 °C to 250 °C from 4.6 to 7.7 % and then decreased to 3.9 % when the temperature decreased to 200 °C. As a result, the catalyst lost 15 % of its initial activity (initial steady state) because of change of temperature (thermal effect on the catalyst).

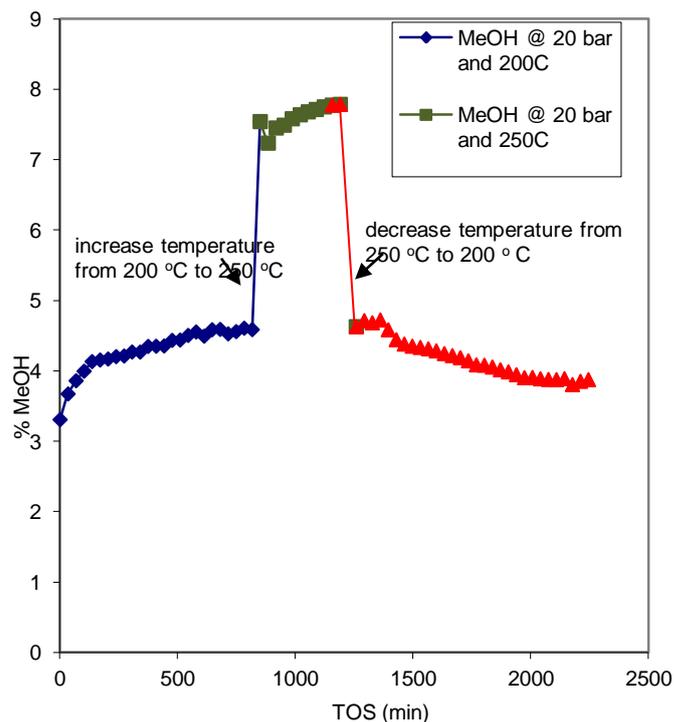


Fig. 5: Effect of temperature changes on CZA catalyst

3.2.3 Effect of Operating Conditions

Table 2 shows the effect of operating temperature and pressure on the activity of CZA catalyst.

Table 2: Effect of operating conditions on CZA catalyst

CZA	run	P (bar)	T (°C)	% MeOH	% MeOH _e	X _{CO} (%)	X _e (%)
1	50	200	200	6	53.3	17	83.2
			250	16	25.3	40	53.9
2	30	208	208	7	35	19.8	69
3	20	200	200	4.6	30.3	12.8	60.8
			250	7.7	7.7	20.5	21.3

From Table 2, it can be seen that for both catalysts the CO conversion and MeOH production decreased with decreasing pressure and increasing temperature, this is due to the nature of MeOH synthesis process which is highly exothermic. The conversion of syngas to MeOH is an exothermic reversible reaction; therefore low temperatures favour higher conversion but this must be balanced against the nature of the catalyst. Also it is clear that the theoretical equilibrium CO conversion (X_e) at different pressures and temperatures. The CZA catalyst showed the highest activity among all the studied catalysts, but this catalyst is active at high temperatures in which the CO conversion ($X_{CO}=20.5\%$) reached the equilibrium conversion ($X_e=21.3\%$) @ 250 °C and 20 bar but it is far away ($X_{CO}=6.2\%$) from the equilibrium conversion ($X_e=60.8\%$) at 200 °C and 20 bar.

3.3 Effect of Addition of 1% Au/CeZrO₄ Catalyst to CZA Catalyst on the MeOH Production

The purpose for the of addition of Au/CeZrO₄ catalyst to CZA catalyst was to promote and enhance the water gas shift reaction step in MeOH synthesis and thus enhance the direct DME synthesis from syngas. Fig. 6 shows the effect of addition of gold based catalyst to CZA catalyst on the MeOH production. A physical mixing of 1% Au/CeZrO₄ and CZA catalyst with 1:1 ratio was used, it is seen from the figure that the addition of gold based catalyst has no effect on promotion the methanol synthesis process.

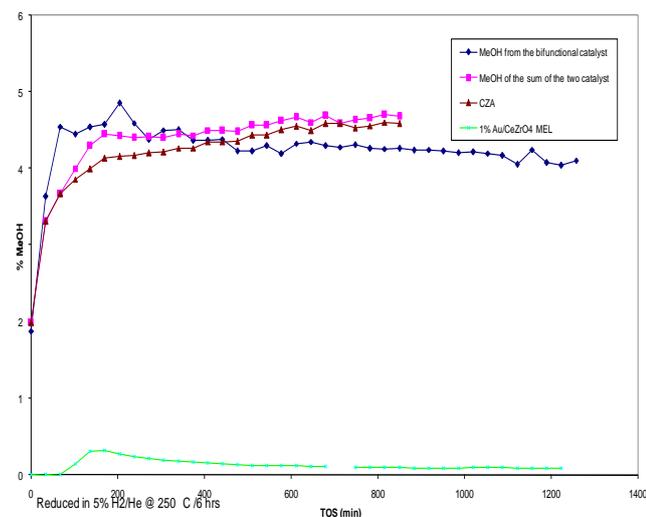


Fig. 6: % MeOH of admixed catalyst of 1% Au/CeZrO₄ and CZA @200 °C and 20 bar

3.2 CATALYST CHARACTERIZATION

3.2.2 Characterization of the CZA catalyst

Fig. 7 shows the in situ XRD patterns of the CZA catalyst during reduction under 5% H₂/He for 6 hrs. Analysis of this suggests a CuO phase ($2\theta = 35.2, 38.5^\circ$) and very weak reflections due to the ZnO phase ($2\theta = 31.8, 36.2^\circ$) and the CuO and ZnO peaks are not finely resolved. The CuO peaks in the fresh catalyst disappeared after (1) hr exposure to the gas mixture and metallic Cu became the main phase of copper and ZnO remains unchanged and ZnO peaks are resolved from CuO peaks. The peaks at 43.4 and 50.3° of the reduced catalyst are attributed to metallic copper.

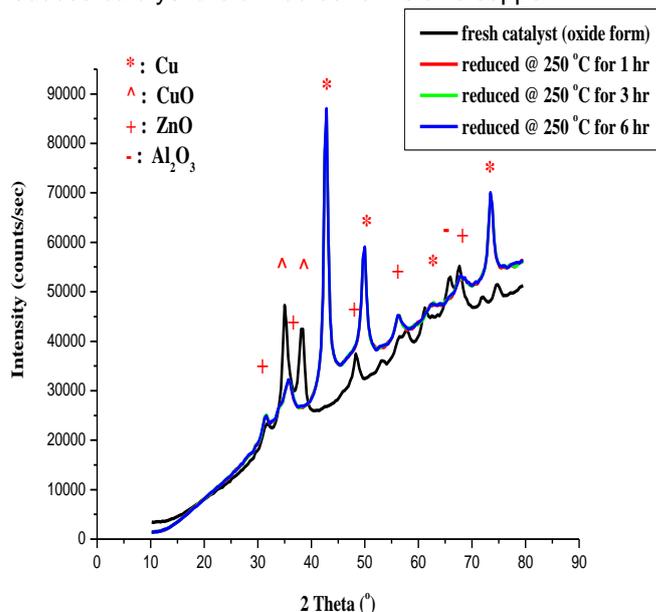


Fig. 7: In situ XRD patterns of CZA catalyst during reducing treatment by 5% H₂/He

4. CONCLUSION

Methanol synthesis was studied over a series of methanol catalysts (CZA, Cu/CeO₂, CuO/MnO/ZnO, 1% Au/CeZrO₄, 5% Pd/Al₂O₃ and physical mixing with ratio 1:1 of (1% Au/CeZrO₄ and CZA)) were prepared and tested for methanol synthesis at different operating conditions: T=200-260 °C, P=20-50 bar, H₂/CO molar ratio=2/1, GHSV=2640 mlg⁻¹h⁻¹. Based on the results, it was found that CZA showed the highest activity and it is the best catalyst for methanol synthesis. Moreover, it was found that the CZA catalyst is stable during the temperature change just 16% of its initial activity (initial steady state) was lost because of the change in temperature.

In-situ XRD of the CZA catalyst showed that CuO peaks in the fresh catalyst disappeared after (1) hr exposure to reduction mixture and metallic Cu became the main phase of copper. As a consequence, the CZA catalyst is easy to reduce.

The addition of 1% Au/CeZrO₄ to CZA catalyst has no effect on promotion the methanol synthesis process. Furthermore, 1% Au/CeZrO₄ catalyst showed fast

deactivation in MeOH synthesis under MeOH reaction conditions which starts after 150 minutes on stream. However, 1% Au/CeZrO₄ catalyst showed higher activity in WGS when compared to a CZA catalyst.

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