

Cyclic Regeneration of Cu/ZnO/Al₂O₃ Nano Crystalline Catalyst of Methanol Steam Reforming for Hydrogen Production in a Micro-Fixed-Bed Reactor

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ABSTRACT: *Hydrogen can be produced for fuel cell applications by using methanol steam reforming reaction. In this article, a method was developed for regeneration of accelerated deactivated methanol-steam-reforming catalyst. Successive deactivation–regeneration cycles were studied in a 250 hours test for the first time including 6 regeneration cycles. It is shown that regeneration of the catalyst in diluted O₂ results in dramatic enhancements of the methanol conversion and this catalyst could be regenerated to near fresh activity. Cokes that can deactivate the catalyst will be burned out in presence of oxygen at the regeneration step. XRD, TGA/DTG, TPR, N₂O Chemisorption, TPO and SEM techniques were used for a complete catalyst characterization. Effects of temperature, water to methanol ratio, concentration of diluted oxygen, CuO/ZnO ratio and adding oxygen along with or without the main feed were also studied by a set of six experiments with duration of 100 h for each to provide a complete know-how on the developed method of regeneration.*

KEY WORDS: *Methanol steam reforming, Fuel cell, Hydrogen, Catalyst, Deactivation, Regeneration.*

INTRODUCTION

Supplying of electrical power for portable devices is still a challenge. Batteries need to be changed or recharged frequently. Fuel cells as an alternative for batteries may operate continuously with low pollutions. Proton Exchange Membrane Fuel Cells (PEMFCs) use hydrogen and oxygen to produce electricity. Oxygen

is easily provided from air; however, hydrogen should be produced from high volumetric energy density and portable fuel sources such as methanol. Thus, hydrogen production for portable fuel cells is of great interest.

Hydrogen is a small molecule with high diffusivity and is considered as an explosive gas. Its storage in high

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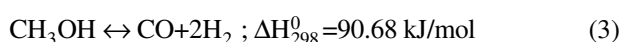
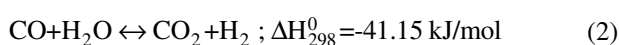
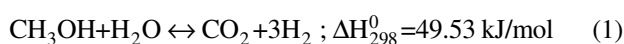
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pressure vessels has a very high risk. Therefore, hydrogen production on-board at atmospheric pressure and low temperatures is an attractive idea for answering the increasing demand of the market for use in fuel cells.

Fuel processing technologies convert a hydrogen containing material such as gasoline, ammonia, or methanol into a hydrogen rich stream. Methanol has higher possible theoretical efficiency between wide ranges of fuels [1, 2]. Hydrogen production from methane, as compared to methanol has three main problems for portable purposes [3]: high reaction temperature, producing large amount of carbon monoxide which is a poison for PEMFC membrane, and finally methane is gas and gas storage is more difficult than liquid storage for portable devices. Methanol steam reforming seems to be beneficial for portable applications because of low reaction temperature, production of much lower carbon monoxide and ease of its transportation and storage as compared to methane reforming.

Steam reforming of methanol has been extensively studied on Cu/ZnO/Al₂O₃ catalyst [4]. This catalyst is also used for both methanol production from synthesis gas [5] and low temperature water gas shift reaction [3]. One of the main problems of Cu-based catalysts is their deactivation by sintering and coking [4]. Some research groups have tried to replace Cu-based catalyst by other metals such as Pd. However, Pd-based catalysts increase the reaction temperature and the carbon monoxide content of the product via methanol decomposition reaction [6].

The main reaction of methanol and water feed on copper catalysts is steam reforming which is an endothermic reaction, according to Eq. (1). Water gas shift reaction changes the CO/CO₂ and H₂/H₂O ratios according to Eq. (2). The rate of Methanol decomposition, as an undesirable and highly endothermic reaction, increases at higher temperatures. This reaction produces carbon monoxide which is a poison for PEMFCs and also produces hydrogen with a low stoichiometric coefficient of 2 instead of 3 in comparison to the methanol steam reforming reaction. Eq. (1) is sum of Eqs. (2) and (3) [7]:



In two recent review articles [4, 8], the performance of several methanol steam reforming catalysts including their deactivation behavior have been reviewed. Gunter et al. [9] had investigated the redox behavior of CuO/ZnO catalyst but with short period of reduction-oxidation cycle, i.e. less than 2 h. Quincoces et al. [10] studied the reduction and regeneration conditions on activity of CuO/ZnO catalyst but for water gas shift reaction not methanol steam reforming. In general, the number of publication on methanol steam reforming as compared to methanol synthesis is much less. Twigg et al. [11] reviewed the deactivation of copper-based catalyst for methanol decomposition, methanol steam reforming and methanol synthesis. Sintering, poisoning and coke formation are proposed as the causes of catalyst deactivation.

In this article, for the first time the cyclic regeneration of methanol steam reforming catalyst was studied by a long time continuous test. A method was developed for catalyst regeneration to near fresh activity and effect of some important parameters (temperature, water to methanol ratio, concentration of diluted oxygen, CuO/ZnO ratio and adding oxygen along with the main feed) on the deactivation-regeneration cycles was studied experimentally for the first time. A complete catalyst characterization studies were performed by using XRD, TGA/DTG, TPR, N₂O Chemisorption, TPO, SEM techniques.

EXPERIMENTS SECTION

Catalyst preparation

CuO/ZnO/Al₂O₃ catalyst was prepared by a co-precipitation method. Cu(NO₃)₂·6H₂O, Zn(NO₃)₂·4H₂O and Al(NO₃)₃·9H₂O (all from Merck) were used as precursors for Cu, Zn and Al respectively. Na₂CO₃ (from Merck) was used as a precipitating agent and for adjusting the pH at 9.0. After dissolving the desired amount of metal nitrate salts in distilled water, sodium carbonate solution was added drop wise such that pH remained constant at about 9.0. The solution of precursor salts was prepared at low concentration, i.e. 0.1 M. The temperature of the precipitation was kept constant at 70 °C. The co-precipitated sample was aged at 70 °C under agitation for 2 h to allow completion of the reactions. The precipitate was then washed with plenty of distilled water to remove sodium ions, collected on a filter and dried at 110 °C for 12 h. The dried sample was calcined

in presence of air in a furnace with temperature ramp rate of 5°C/min from 30 to 350°C, maintained at 350 °C for 3.5 h and cooled down to room temperature overnight. The catalyst was pressed, crushed and sieved to obtain a particle size between 125 to 250 μm. A CuO/ZnO/Al₂O₃ catalyst with composition of 64/24/12 and another one with 24/64/12 weight percentages are prepared in this way.

Catalytic activity measurements

The setup for measuring the performance of catalysts and the details of the reactor inside of a furnace with two zones were illustrated in Fig. 1.a and b, respectively. Two mass flow controllers (Brooks Instrument) were used to control the flow rates of gases, i.e. H₂, N₂ and O₂ (all 99.999% purity) used for reduction and regeneration of the catalyst. The gases are mixed in a packed column as a pre-mixer, before entry into the reactor. The micro reactor is loaded with small amount of catalyst, 200 mg. The catalyst is placed between two layers of quartz wool. A layer of carborundum (silicon carbide) grains that are inert for this reaction is used as vaporizer and is located on top of the catalyst layer. Using the smaller 1/4" OD tube downstream of the reactor helps to remove the product rapidly from the hot zone of the reactor. A syringe pump (Atom, Japan) was used for precise pumping of liquid feed, i.e. methanol/water mixture. Methanol with 99.9% purity and deionized water was used for feed. A 1/16" OD diameter stainless steel tube was used to transport liquid feed from syringe pump into the reactor. This tube continues into the reactor and ends up inside the carborundum zone to ensure complete vaporization of liquid feed and prevent dead zones for liquid and remove the liquid drops which cause a pulsating flow.

A K-type thermocouple was placed inside the catalyst bed to monitor its temperature. The reactor was located in an electrical furnace which has two zones: the first zone for pre-heating and vaporization and the second zone for reaction. The effluents from the reactor can either go to the condenser for removing the condensate (unconverted water and methanol) or can go with a heated traced-line directly to the Gas Chromatography (GC). Heated traced-lines were used to prevent condensing vapors which can plug the lines and increase the reactor pressure.

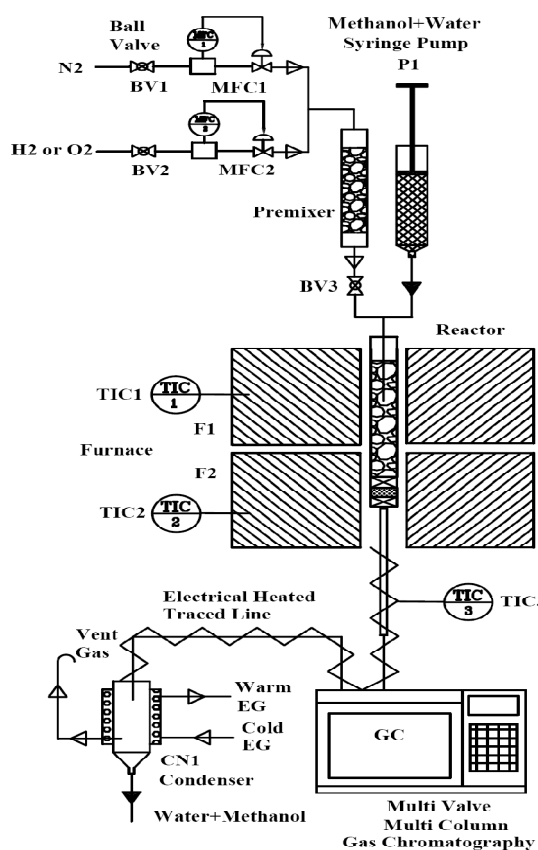
Procedure of Long time deactivation-regeneration cycles

Lee et al. [12] used a commercial Cu/ZnO/Al₂O₃ catalyst, (Synetix 33-5) in the kinetic experiment with the following composition 64 wt.% CuO, 24 wt.% ZnO, 10 wt.% Al₂O₃ and 2 wt.% MgO. We synthesized the same catalyst without MgO and 12% Alumina to accelerate the deactivation rate. As, it was released in the General Catalogue of Sud Chemie Catalyt of year 2007, commercial methanol steam reforming catalyst (ReforMax[®]M) of Sud Chemie has near the same composition of CuO/ZnO/Al₂O₃ 66/23/11 wt%. Also, they used nitrogen for dilution of the feed and higher molar ratio of water to methanol (about 2). In our work again for accelerating the deactivation, inert gas was not used and water to methanol molar ratio is only 1.1. They also used lower temperature, 210 °C, which is too low in comparison to our temperature 280 °C. The deactivation of their catalyst can be tracked in the Fig. 1 of their article that shows conversion loss from about 85 to 40 after 120 h at 210 °C with 55% N₂ in the feed.

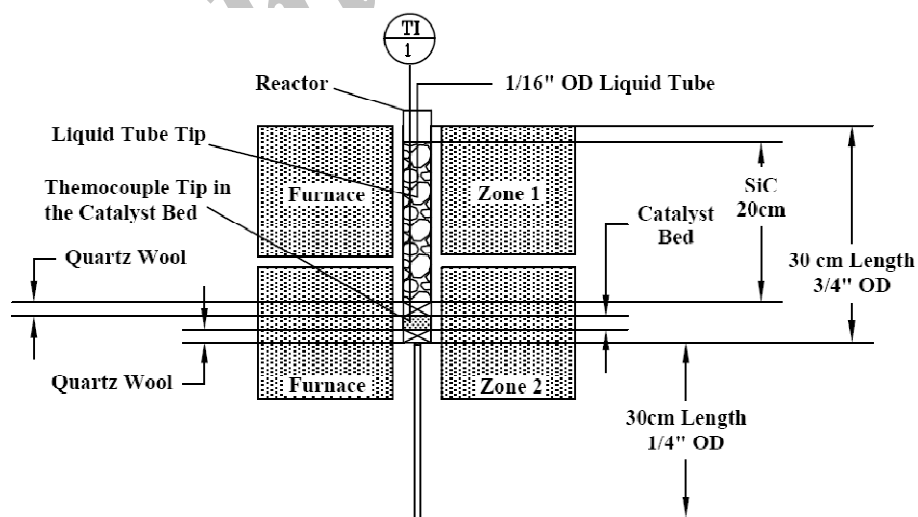
A long time test was considered to study the deactivation-regeneration cycles. In this experiment, CuO/ZnO/Al₂O₃ (64/24/12 wt %) was reduced in 20% H₂ in N₂ mixture. Then it was deactivated for two days in a steam reforming reaction condition by a liquid feed flow rate of 2 ml/min and feed water/methanol ratio of 1.1 at 280 °C. After deactivation for two days, the reactor was purged by N₂ for 35 minutes by a high flow rate of 400 sccm and then regenerated by 50 sccm of a mixture containing 5% O₂ in N₂ in the cycle 1. In the cycle 2, the oxidized catalyst was reduced by the feed and it was deactivated for two days. The cycle 3, 4 and 5 are the same as cycle 2 but the deactivation period is one day instead of two days. In cycle 6, the deactivation period is near 3 days and after that the catalyst was deactivated for near 1 day. Methanol conversion and hydrogen selectivity percent, $100 \times F_{H_2} / (F_{H_2} + F_{H_2O})$, at the exit of the reactor, in this cycles were calculated. F indicates molar flow rate of an indexed component. For comparison, a 100 hours test was repeated without regeneration.

Procedure of parametric study on deactivation-regeneration cycles

In all sets of parameter studying, first reduction and feed conditions was the same as section 2.2.1 but the procedure contains cycle 1, 2 and 3 with 48, 24 and 24 h



a. The setup for measuring the performance of catalysts



b. Details of the reactor inside of two zone furnace

Fig. 1: Schematic figure of catalyst activity test setup and the reactor details.

deactivation, respectively. Before regeneration, a 35 min. purging procedure was done in all sets except one set that is the set which the feed was not stop during the regeneration cycle. Then, one hour regeneration program by lean oxygen stream (5% O₂ in N₂) was performed on the catalyst with changing of some parameters. After first regeneration, the catalyst was reduced by feed stream in situ, because the methanol/water feed, is itself reducer and produces hydrogen that is reducer again. The temperature was selected as high as 280-300 °C, the water to methanol as 1.1 and 2, the fine catalyst in a mesh between of 60-120 and high conversion conditions is used to accelerate the deactivation. For this purpose, the feed was not diluted with an inert gas.

Gas Chromatograph

In these experiments, online analyses of the hot reactor effluent are performed for direct calculation of methanol conversion. GC Agilent 6890 equipped with a Thermal Conductivity Detector (TCD), a Flame Ionization Detector (FID), 1 ml sample loop and two 6-port chromatographic valves (Valco valve): one for gas sampling and the other for switching between two 1/8 inch OD packed columns of Porapak-Q (4m, Mesh 80/100) and molecular sieve 13X (2m, Mesh 80/100). A methanizer with a 5.0 wt% Ru/SiO₂ catalyst was used in this GC to convert CO, CO₂ to methane in order to be analyzed with FID detector because of higher detection limit of FID as compared to TCD. Argon was used as the carrier gas to detect hydrogen. GC oven has a special temperature program between 40 and 160 °C.

Characterization

XRD

The X-ray diffraction patterns of the catalyst samples were obtained by a Philips PW 1740 (Cu Kα1 radiation, λ = 1.54056 Å) in a 2θ range of 5–90° at 40 kV, 20 mA with scanning rate of 0.5°/min. The crystallite size was estimated according to Scherrer's equation which is limited to nano-scale dimensions.

$$dc = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

Where dc is the mean size of the ordered (crystalline) domains which may be smaller or equal to the grain size. K is the dimensionless shape factor which has a typical

value of about 0.9, λ is the x-ray wavelength, β is the line broadening at half the maximum intensity in radians 2θ, and θ is the Bragg angle [13, 14].

TGA/DTG

Thermal Gravimetric Analysis (TGA) pattern of each sample was measured by TGA851e (Mettler Toledo GmbH, Switzerland) in an air stream of 50 sccm⁽¹⁾ with a temperature ramp rate of 5°C/min from 50 to 600°C.

TPR

Temperature-Programmed Reduction (TPR) spectrum was recorded by monitoring H₂ consumption using TCD. It was performed by the Bel-Cat Instrument. About 100 mg of the catalyst samples were heated from 30 to 350 °C at a rate of 5 °C/min in 6.5% H₂/Ar with flow rate of 50 sccm. During the TPR measurement, produced water was removed through a column of dried molecular sieve 13X which was placed between the sample and the TCD.

N₂O titration

N₂O titration was used for measuring copper surface area and its active phase dispersion. This measurement was performed by Advanced Model Bel-Cat Catalyst Analyzer (Bel Japan, Inc.) First TPR was performed by increasing the temperature from 30 to 350 °C with slope of 5 °C/min in a stream of 6.5% H₂ in Ar with flow of 50 sccm. In the first TPR process, CuO in the catalyst sample converts to Cu [15, 16]. After the first TPR, the sample cools down to a N₂O-oxidation temperature of 65°C and then by N₂O chemisorption at 65°C for 60 min, it was assumed that only surface Cu converts to Cu₂O (Cu I) that is active site subject to reaction of Eq. (5) [15, 16].



After N₂O titration, all Cu₂O (Cu I) converts to Cu (Cu 0) by second TPR with rising the temperature from 65 to 350 °C with the rate of 5 °C/min in a stream of 6.5% H₂ in Ar at flow rate of 50 sccm.

The peak area of the first TPR profile (A₁) corresponds to the amount of all CuO in the sample, and that of the second TPR (A₂) is the amount of Cu₂O produced by N₂O oxidation. A fraction of Cu₂O in the total Cu, D*, is calculated as D* = 2A₂/A₁, which

(1) Standard cubic centimeter per minute

correspond to apparent Cu dispersion [15, 16]. If N_2O oxidizes only the surface of Cu, D^* is regarded as the true dispersion (D) defined as the ratio of exposed surface Cu to total Cu. Thus, the Cu metal surface area per unit weight of catalyst, S_{Cu} , can be calculated from Eq. (6) [15, 16]:

$$S_{Cu} \text{ (m}^2\text{/gcat)} = D \times A_v \times \text{Wt\%Cu} / (100 \times MW_{Cu} \times N_{Cu}) \quad (6)$$

where A_v is Avogadro's number (6.02×10^{23}), Wt\%Cu is Cu content (wt%) of the catalyst, MW_{Cu} atomic weight of Cu (63.5 g/mol), and N_{Cu} is number of surface Cu atoms in unit surface area. A reported N_{Cu} value of $1.7 \times 10^{19} \text{ m}^{-2}$ [17] was used for the calculation of S_{Cu} , while N_{Cu} values in the range $(1.68\text{--}1.35) \times 10^{19} \text{ m}^{-2}$ are available for different Cu crystal planes [18].

TPO

Temperature-Programmed Oxidation (TPO) test of the deactivated catalyst according to [19, 20] was performed by loading 100 mg of the sample in a quartz tube reactor with 5 mm ID to study the amount of carbon containing material formed on deactivated catalyst and its resistance to combustion. TPO feed gas was 2% O_2 in N_2 with flow rate of 80 sccm. The reactor was placed inside a tubular furnace equipped with a temperature controller. A K-type thermocouple was inserted inside the catalyst bed and a temperature ramp rate of $10 \text{ }^\circ\text{C}/\text{min}$ was regulated to change the temperature from 30 to $900 \text{ }^\circ\text{C}$. An online Fourier Transform Infra Red (FT-IR) was used for analyzing the reactor effluent gas sample. FT-IR spectra of CO_2 and CO produced from the coke oxidation were instantaneously recorded. Bruker Vector22 spectrometer FT-IR was equipped with a DTGS detector and a 2.0 cm ID and 10.0 cm length gas cell with KBr windows. Transmission mode, resolution of 5 cm^{-1} , averaging of scanning repetition of 10 in 60 seconds and frequency range of 4000 to 400 cm^{-1} was used for the measurement. Peak areas in the ranges of $2400\text{--}2280 \text{ cm}^{-1}$ and $2235\text{--}2030 \text{ cm}^{-1}$ are used for CO_2 and CO , respectively. The FTIR was calibrated by 2000 ppm CO_2 and there was not any peak for CO in deactivated catalyst of this study.

SEM

Scanning Electron Microscopy (SEM) was performed by a Philips XL30 instrument to investigate the particle size and morphology of the catalysts.

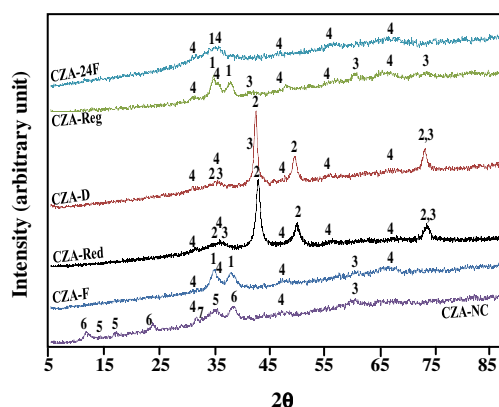


Fig. 2: XRD patterns of CZA catalysts (1- CuO monoclinic, 2- Cu cubic, 3- Cu_2O cubic, 4- ZnO hexagonal, 5- Malachite $Cu_2(OH)_2CO_3$, 6- Hydrotalcite $Cu_2Zn_4Al_2(OH)_6CO_3 \cdot 4H_2O$, 7- Aurichalcite $(Cu,Zn)_5(OH)_6(CO_3)_2$).

RESULTS AND DISCUSSIONS

Characterization discussion

XRD

The XRD patterns of not calcined (CZA-NC), freshly calcined (CZA-F), reduced catalyst (CZA-Red), deactivated (CZA-D), and regenerated (CZA-Reg) catalyst of 64/24/12 (base composition) $CuO/ZnO/Al_2O_3$, and freshly calcined catalyst with 24/64/12 weight percentages for $CuO/ZnO/Al_2O_3$ (CZA-24F) were illustrated in Fig. 2. The catalysts are deactivated by steam reforming of methanol with water/methanol molar ratio of 1.1 at $280 \text{ }^\circ\text{C}$ for 2 days and passivated in 5% O_2 at $25 \text{ }^\circ\text{C}$. Using Scherrer's equation, the crystal size of Cu or CuO was calculated and listed in Table 1.

XRD pattern of CZA-NC and its comparison with standard peaks of JCPDS cards shows that CZA-NC consists of Malachite crystal with composition of $Cu_2(OH)_2CO_3$ (JCPDS 41-1390) and Hydrotalcite crystal with composition of $Cu_2Zn_4Al_2(OH)_6CO_3 \cdot 4H_2O$ (JCPDS 38-0487) but Aurichalcite crystals with composition of $(Cu,Zn)_5(OH)_6(CO_3)_2$ (JCPDS 09-0492) was not detected significantly. Because of drying at temperature of $110 \text{ }^\circ\text{C}$, maybe some ZnO and CuO crystals were produced but their concentrations are low and thus the peak intensities which correspond to ZnO and CuO crystals are not considerable.

XRD Pattern of CZA-F shows the present of CuO and ZnO crystals while Al_2O_3 crystals could not be distinguished. Alumina may be in amorphous form. Also, no Cu_2O detected peaks are observed in the XRD pattern of CZA-F.

Table 1: Comparing of characteristics results for different catalysts.

| Property | CuO Crystallite Size, (nm) | Cu Crystallite Size (nm) | Cu Surface Area (m ² /g) | Cu Dispersion (%) | Cu Particle size (nm) | Carbon Content (%) |
|-----------|----------------------------|--------------------------|-------------------------------------|----------------------------|--------------------------------|--------------------|
| Test Cat. | XRD | XRD | N ₂ O Titration | N ₂ O Titration | From S _{Cu} , Sphere* | TPO |
| CZA-F | 6.4 | No Peak | 48.5 | 14.8 | 8.1 | - |
| CZA-Red | No Peak | 8.5 | - | - | - | - |
| CZA-D | No Peak | 9.4 | - | - | - | 0.68 |
| CZA-Reg | 7.0 | No Peak | 43.3 | 13.2 | 9.1 | - |
| CZA-24F | ~1.3** | No Peak | 86.4 | 77.1 | 1.6 | - |

* Calculation from Cu surface area by assuming spherical particles and copper skeleton density (ρ_{Cu}) of 8960 kg/m³ according to the formula $dp_{Cu} = 6 \times (Wt\%Cu/100) / (\rho_{Cu} \times S_{Cu})$ in SI units.

** Roughly approximated.

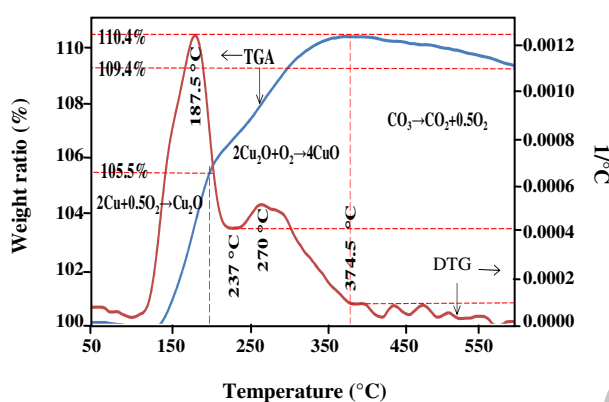


Fig. 3: TGA/DTG diagram of deactivated catalyst (CZA-D).

CZA-RED XRD pattern shows an intensive Cu and ZnO peaks and minor peaks for Cu₂O which possibly formed during the passivation. Cu with crystallite size in a nano meter range can be an active phase in the catalyst and it can be seen that on the reduction of catalyst, copper oxide reduced to the copper while zinc oxide remained in oxide form. CZA-D included Cu, Cu₂O and ZnO crystals like CZA-Red but all the peaks in deactivated catalyst has less line broadening at half the maximum intensity, but it can not be concluded that the deactivated catalyst has larger crystallite size than the fresh reduced catalyst. Because the difference is not significant. CZA-Reg has CuO, Cu₂O and ZnO crystals and CuO has more distinguishable peaks than Cu₂O. Because lower concentration of oxygen is better for regeneration stream, so detecting more Cu₂O in the regenerated catalyst is more desirable. Comparing CZA-Reg with CZA-F shows that regenerated catalyst has larger crystal size than the fresh one. But the difference is not significant. Finally,

the diffractogram peaks of CZA-24F can mainly be assignable to CuO and ZnO crystals.

TGA/DTG

The TGA/DTG diagram of deactivated CZA-D catalyst in an air stream is shown in Fig. 3. The diagram shows two sharp increases in the catalyst sample weight, which correspond to the DTG peaks at 187.5 °C and 270 °C, respectively. This may indicate progressive oxidation of copper to Cu₂O and CuO. Oxidizable coke content of the deactivated catalyst in comparison to copper content is very low, so TPO test was needed for estimating the coke percent and the coke content don't change the TGA curve significantly. A decrease in the sample weight in TGA diagram at temperatures higher than 374.5 °C may be attributed to decomposition of carbonate group. Because the calcination temperature was 350 °C and some carbonate (from precipitating agent that is sodium carbonate) may not be removed from the catalyst.

H₂-TPR

H₂-TPR profiles of the catalyst samples are shown in Fig. 4. The fresh catalyst (CZA-F) shows a major TPR peak at 228 °C and two minor shoulders at 160-205 °C and 255-300 °C. The deactivated catalyst (CZA-D) shows a small peak at 199 °C, about 30 °C lower than the fresh major TPR peak temperature. The deactivated catalyst is reduced in situ and its surface layers are oxidized by passivation in 5% O₂ in N₂ at 25 °C. The short time regeneration of the catalyst in 5% O₂ in N₂ at reaction temperature of 280 °C for 60 min has oxidized the CAZ-Reg catalyst. A small TPR peak of CZA-24F at 223 °C, corresponds to its lower Cu content.

N_2O titration

The results of copper surface area and copper dispersion were reported in Table 1 and TPR after N_2O chemisorption is shown in Fig. 5 for base catalyst in the form of fresh (CZA-F), deactivated (CZA-D) and regenerated (CZA-Reg) and also another fresh catalyst (CZA-24F) with composition of 24/64/12 weight percent for $CuO/ZnO/Al_2O_3$.

In Fig. 5, TPR results after N_2O Chemisorption show peak temperature of 162, 164, 154 and 160 °C for CZA-F, CZA-D, CZA-Reg and CZA-24F, respectively. It illustrates that peak of regenerated catalyst (CZA-Reg) shifted to lower temperature in comparison to peak of fresh catalyst (CZA-F). It means that reduction of dispersed copper oxides in regenerated catalyst by hydrogen is easier than the fresh one. Peak area of CZA-24F is higher than other ones and it indicates more copper dispersion.

TPO

The CO_2 evolution during the TPO of deactivated catalyst sample (CZA-D) is shown in Fig. 6. In this TPO experiment, no detectable amount of CO is formed. The result shows three peaks: first peak between 80 and 310 °C, second peak in the range of 310 to 480 °C and the third peak between 480 and 800 °C. The area of these three peaks have 43.0%, 22.4% and 34.6% sharing in the total TPO peak area which is equal to 563.5 μmol of CO_2 per gram of catalyst or 0.68 percent of carbon per gram of catalyst. The peaks may be ascribed to different carbonaceous type or can be attributed to location of the same carbonaceous material in catalyst sites.

Existence of carbon containing materials was confirmed by XPS study of Agarwal *et al.* [21] and the TPO peak between 480 and 800 °C may be related to carbonate decomposition because of existence of decreasing TGA curve at such temperature range of Fig. 3.

It is reported that the deactivation of CuO/CeO_2 during steam reforming of methanol is caused by coke deposition which gives a CO_2 peak around 200 °C (Starting from 100 °C and maximize at 200 °C) on TPO [22]. First peak of Fig. 6 is around 200 °C and it is in good agreement with reference [22]. The first peaks of Fig. 6 between 80 and 310 °C cannot be related to carbonate decomposition because of calcinations of the catalyst at 350 °C and it indicates the coke deposition. This coke can be removed by regeneration procedure including adding lean O_2 stream after closing the feed stream.

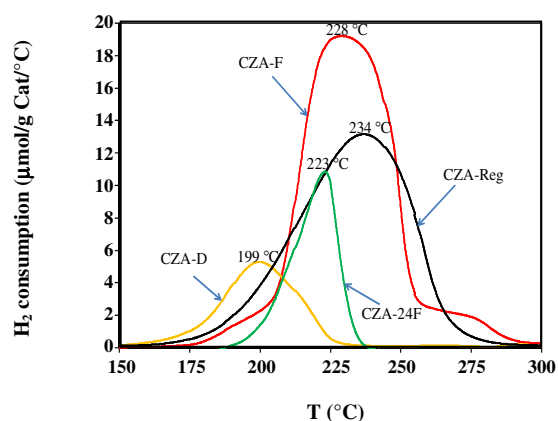


Fig. 4: TPR diagrams of CZA-F, CZA-D, CZA-Reg and CZA-24F samples.

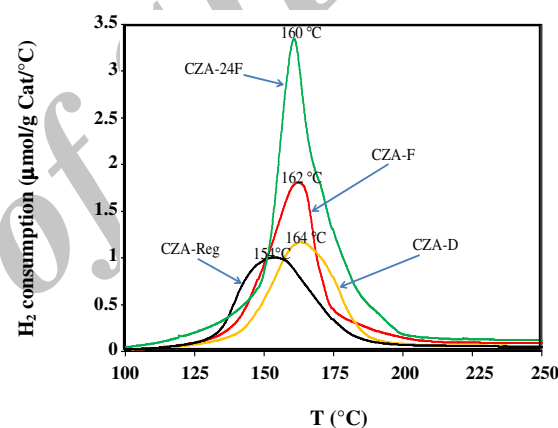


Fig. 5: TPR diagrams of CZA-F, CZA-D, CZA-Reg and CZA-24F samples after 60 min N_2O chemisorption at 65 °C.

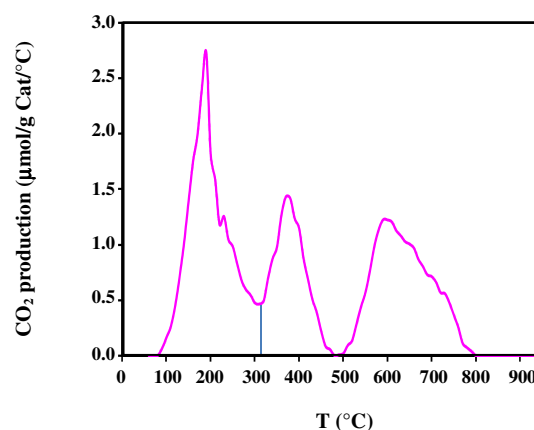
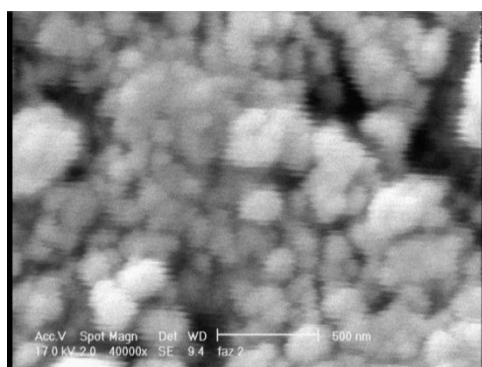
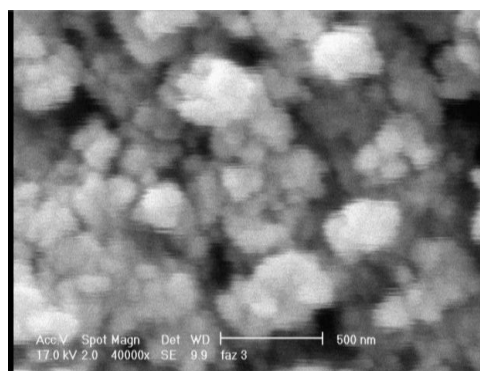


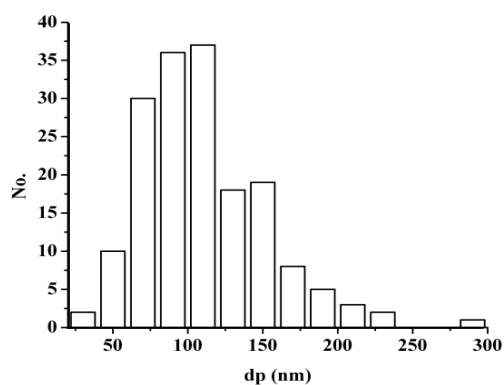
Fig. 6: TPO diagrams of deactivated catalyst (CZA-D).



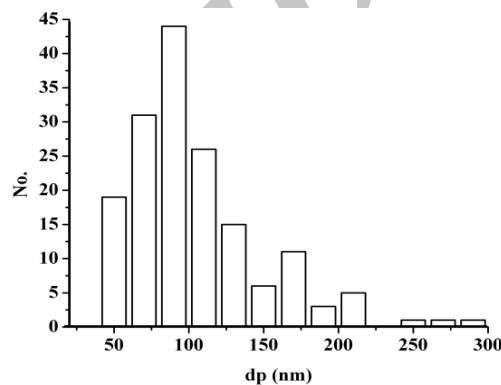
a. CZA-D



b. CZA-Reg



c. CZA-D, agglomeration size histogram



d. CZA-Reg, agglomeration size histogram

Fig. 7: SEM image of deactivated catalyst (CZA-D) and regenerated catalyst (CZA-Reg).

SEM

The SEM image of deactivated catalyst (CZA-D) and regenerated catalyst (CZA-Reg) is shown in Fig. 7. Also, Agglomeration size histogram of CZA-D and CZA-Reg is reported in this figure. Image processing of CZA-D and CZA-Reg catalysts show that, these co-precipitated catalysts consist of small agglomerations in the range of 30 to 300 nm.

Long time deactivation-regeneration cycles

Figs. 8 and 9 show methanol conversion and hydrogen selectivity during the deactivation and regeneration cycles of 200 mg CZA-F catalyst at 280 °C with liquid feed flow rate of 2 mL/min and feed water/methanol ratio of 1.1. The catalyst is deactivated during 1-3 days and regenerated for 60 min. During

1-3 days on steam reforming of methanol, the catalyst significantly deactivates. The regeneration in 5% O₂ in N₂ brings back the catalyst activity to slightly lower than that of the previously regenerated one. Deactivation of the catalyst occurred in 1-2 days may be regenerated by the procedure employed. In this set, an increase of two fold in methanol conversion was observed. The deactivated catalyst has significantly lower hydrogen selectivity (Fig. 9.a). After each regeneration, the hydrogen selectivity returns back to that of the fresh catalyst. This corresponds to up to about 30% enhancement of the hydrogen selectivity in 1-2 days deactivations. The results of Table 1 (Cu crystalline size of CZA-Red and CZA-D) show that deactivated catalyst has slightly larger Cu crystal size than the freshly reduced one that is not significant because of error of calculation by Scherrer's equation.

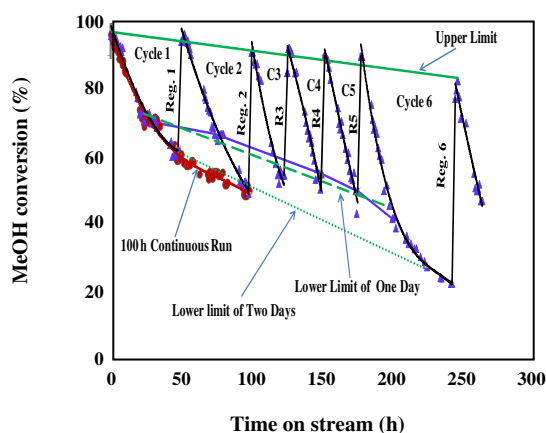


Fig. 8: Methanol conversion in reaction-regeneration cycles.

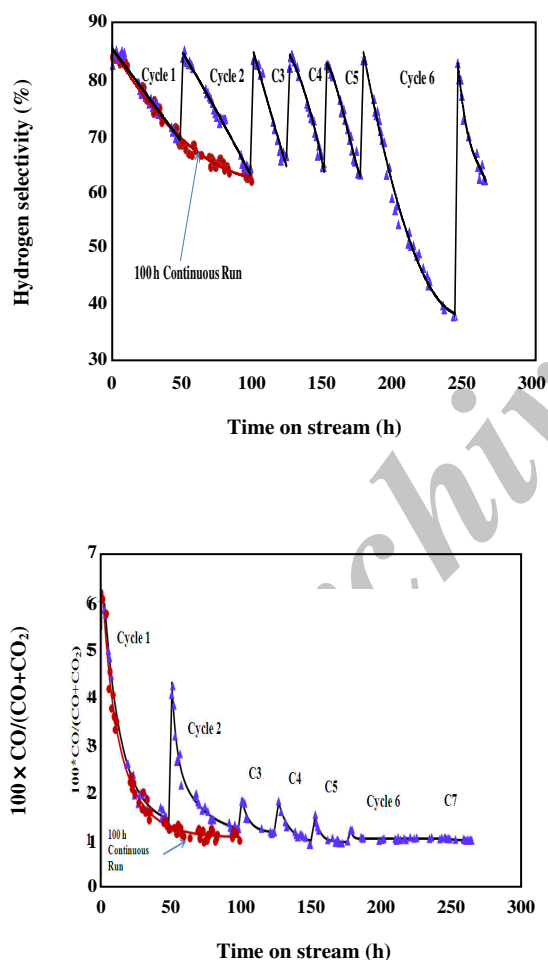


Fig. 9: a) Hydrogen selectivity in reaction-regeneration cycles.
b) Carbon monoxide selectivity in reaction-regeneration cycles.

It indicates that activity loss is not affected significantly by sintering during one deactivation- regeneration cycle after 2 days.

The CO selectivity percent, in relation to CO_2 was defined as $100 \cdot F_{\text{CO}} / (F_{\text{CO}} + F_{\text{CO}_2})$. CO selectivity for cycles of reaction and regeneration was plotted in Fig. 9.b by triangle data points. In this figure, also CO selectivity for an 100 hours continuous run was plotted with circle data points. The data shows that CO selectivity of Cycle 1 was dropped by spending the time. At start-up of the reaction, CO concentration is high and according to Boudouard reaction ($2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$), the coke formation is high. After the first regeneration, the CO selectivity increased to a value lower than the initial point of the first cycle and then decreased in an exponential decay curve. In cycle 3, 4, 5 and 6, the increase in the CO selectivity after regeneration was reduced and finally after regeneration of cycle 6, there is not a peak after regeneration and CO selectivity was remained constant.

Effect of parameters on deactivation-regeneration cycles

For studying the effect of some parameters, six tests during about 100 h with two reaction-regeneration cycles were considered and the parameters were changed according to design of experiment listed in Table 2.

The methanol conversions in six sets of experiments are presented in Fig. 10. Set 1 was used as a base for comparison. The declines and enhancements in methanol conversion following deactivation and regeneration cycles are summarizes in Table 3.

Temperature

The conditions in Sets 2 and 3 are the same expect for the reactor temperature. It should be noted that in all of the experiments, the reactor temperature is the same as regeneration temperature. As it may be observed from Fig. 10 by increasing the temperature from 280 to 300 °C, in spite of a small enhancement in initial methanol conversion at 300 °C compared to that of 280 °C, the rate of deactivation is quite higher at 300 °C. It is interesting that in Set 2 the catalyst with more deactivation gained higher activity improvement following the regeneration. However, the absolute activity obtained for the set at lower temperature is higher. Thus, it may be concluded that lower temperature is more suited for regeneration by lean oxygen flow.

Table 2: Experimental design for parametric study.

| No | Name | Catalyst | Reforming Temperature (°C) | H ₂ O/MeOH | %O ₂ | 1st oxidation without Feed |
|----|--------------|----------|----------------------------|-----------------------|-----------------|----------------------------|
| 1 | Set 1 (Base) | CZA-F | 280 | 1.1 | 5 | Yes |
| 2 | Set 2 | CZA-F | 300 | 1.1 | 5 | Yes |
| 3 | Set 3 | CZA-F | 280 | 1.1 | 21 | Yes |
| 4 | Set 4 | CZA-F | 280 | 2.0 | 5 | Yes |
| 5 | Set 5 | CZA-F | 300 | 1.1 | 5 | NO |
| 6 | Set 6 | CZA-24F | 280 | 1.1 | 5 | Yes |

Table 3: Methanol conversions relative decline and enhancement for deactivation and regeneration cycles.

| No | Name | D ₁ % | R ₁ % | D ₂ % | R ₂ % | D ₃ % |
|----|--------------|------------------|------------------|------------------|------------------|------------------|
| 1 | Set 1 (Base) | 38 | 54 | 38 | 55 | 42 |
| 2 | Set 2 | 53 | 82 | 64 | 166 | 64 |
| 3 | Set 3 | 41 | 53 | 46 | 77 | 54 |
| 4 | Set 4 | 28 | 27 | 16 | 16 | 17 |
| 5 | Set 5 | 55 | 0 | 35 | 200 | 46 |
| 6 | Set 6 | 56 | 126 | 48 | 88 | 49 |

$X_1\%$ is the maximum methanol conversion of fresh catalyst

$X_2\%$ is the methanol conversion after 2 days deactivation of fresh catalyst

$X_3\%$ is the maximum methanol conversion after first regeneration

$X_4\%$ is the methanol conversion after one day deactivation after X_3

$X_5\%$ is the maximum methanol conversion after second regeneration

$X_6\%$ is the methanol conversion after one day deactivation after X_5

$D_1\% = 100 \cdot (X_1 - X_2) / X_1$; $R_1\% = 100 \cdot (X_3 - X_2) / X_2$; $D_2\% = 100 \cdot (X_3 - X_4) / X_3$

$R_2\% = 100 \cdot (X_5 - X_4) / X_4$; $D_3\% = 100 \cdot (X_5 - X_6) / X_5$

O₂ concentration during regeneration

Set 1 and 3 are the same but have one difference which is the oxygen mole percent in nitrogen that was used in regeneration stage. In Set 1, 5% oxygen and in Set 3, 21% oxygen was used in mixture with nitrogen. In Set 1 and 3, the conversion curve has the same trend and good matching in first 48 hours. It shows good reproducibility of the data for the same catalyst in the same condition but in different repetitions. Regeneration in Set 3, with the higher oxygen concentration, leads to lower level of conversion peaks in comparison to the base Set, Set 1; i.e., regeneration with air increases the conversion less than Set with 5% oxygen and causes to increase the deactivation rate after the regeneration. So, the low level of oxygen concentration is more suitable than the high one for regeneration of this catalyst and unfortunately air must be diluted more to obtain a better result.

Variation of the temperature of catalyst during regeneration time for Set 1 and Set 3 were illustrated in Fig. 11. In Set 1 with 5% oxygen, the peak of rising of temperature related to copper oxidation is very broad and it takes about 60 min. But in the Set 3 with 21% oxygen, rising of temperature occurs in a narrow peak less than 10 min. Also, the maximum of temperature in high oxygen is more than lower oxygen percent. Copper oxidation is exothermic and produces heat that increase the temperature of catalyst bulk according to Eqs. (7) and (8). Also, small amount of coke will be oxidized at this stage but the mass of coke is very lower than copper content but the heat of coke oxidation is higher. The furnace was turned off by relay action to return the temperature to set points of PID controller and establish isothermal condition but at this condition the heat production of oxidation reaction proceeds against heat loss of insulated furnace and the average temperature of

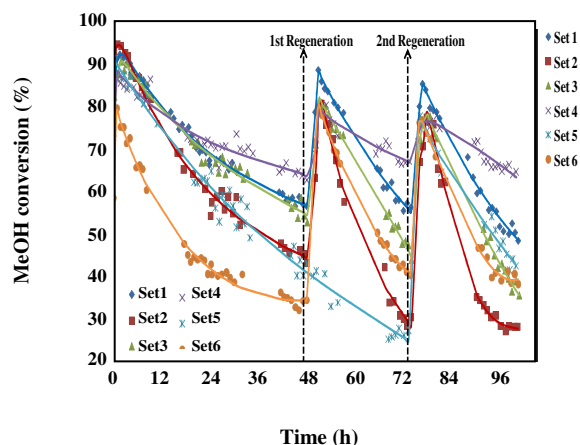
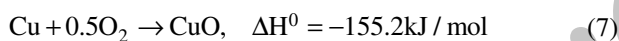


Fig. 10: Effect of parameters on reaction-regeneration cycles in six Sets of about 100h.

catalyst layer increase a little and little increase is more suitable than great increase for regeneration by oxidation. In scaling up the process, if the amount of catalyst is high, the reactor shape and conduction and convection heat transfer in addition to oxygen stream flow rate and concentration will be important to reduce the catalyst temperature rise.



H₂O/Methanol molar ratio

In Set 4, higher amount of water was used in the feed mixture (water and methanol mixture) in comparison to the base Set (the Set 1). In Set 1 and 4, H₂O/Methanol molar ratios are 1.1 and 2.0, respectively. In Set 4, with higher H₂O/MeOH ratio, the amount of deactivation was lower and the effect of regeneration by oxygen was lower too. In Set 4, the conversion peak after regeneration was lower than the base Set. So it can be concluded that higher water to methanol ratio reduces the deactivation and it can discuss the effect of water in decreasing of the deactivation by decreasing the coke formation like the steam reforming of methane. It seems that water can decrease the CO formation by water gas shift reaction and less carbon monoxide decreases the coke formation by Boudouard reaction ($2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$).

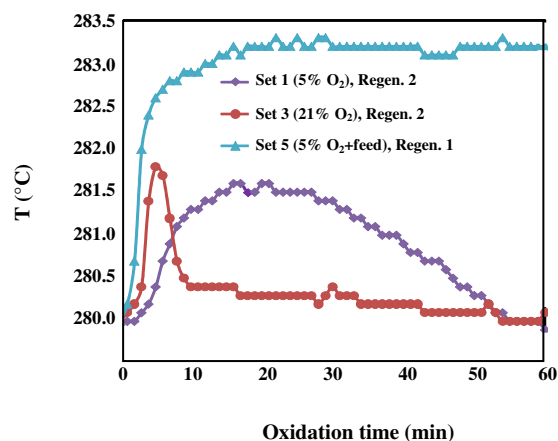


Fig. 11: Temperature of catalyst layer vs. time at regeneration stage.

Adding O₂ without stopping the feed

In experiment of Set 5, after continuous running of the reactor for two days (48 h) a stream of 5% oxygen in nitrogen was allowed to flow through the reactor without stopping the feed and purging the reactor with nitrogen. Since the concentration of oxygen in this set is low and was introduced along with the feed, no catalyst regeneration was occurred. According to the results presented in Fig. 10 in the experiment of Set 1, regeneration of the catalyst did occur although the level of oxygen is similar to the Set 5. The difference in the test conditions in these sets is as follows; in Set 1 after 48 h running the reactor under the feed, feed is stopped and the reactor is purged with nitrogen and a stream of 5% oxygen in nitrogen is introduced into the reactor, whereas in Set 5 the stream of 5% oxygen is introduced after 48 h in presence of the feed and without nitrogen purging in between.

The reactor temperature in this set, i.e. Set 5, of experiment like experiment of Set 2 was 300°C. As is observed in Fig. 10 the methanol conversion curves in the first 48 h for these two sets follow each other, indicating the reproducibility of the results.

The temperatures of the catalyst bed during regeneration for experiment of Sets 5, 1 and 3 are presented in Fig. 11. Comparing the corresponding curves for Set 5 with those for Sets 1 and 3 indicate that addition of 5% O₂/N₂ to the feed although causes oxidative methanol reaction, an exothermic reaction, proceed but because of low level of oxygen, it does not change the oxidation state of the copper. So the temperature

did not return back to the temperature before adding oxygen, in the onset of oxygen addition to the feed. Thus, in order to regenerate the catalyst, the flow of feed to the reactor should be stopped and a lean stream of oxygen needs to be introduced after purging the reactor.

CuO/ZnO ratio

The catalyst in Sets from 1 to 5 was composed of 64/24/12 weight percent which is corresponding to CuO/ZnO/Al₂O₃. But in Set 6, the composition of 24/64/12 was used to change the CuO/ZnO ratio from 2.667 to 0.375. By decreasing the CuO/ZnO ratio in Set 6 in comparison to the base Set, Set 1, the percent of copper reduces and it leads to lower methanol conversion because of deficiency of active phase. Also, by increasing the ZnO in the catalyst mixture, the deactivation rate was not changed significantly.

Sintering and coke formation

Cu/ZnO/Al₂O₃ catalyst for methanol steam reforming may be deactivated because of sintering of Cu nano clusters and coking [23]. Increasing of water/methanol ratio in the feed results in less deactivation rate as is depicted in Fig. 10. So it concludes that water reduces the coke formation. *Cao et al.* [24] reported deactivation by the coke formation when water was absent in the feed. *Valdes-Solis et al.* [23] showed that the increase of steam to carbon ratio is also favorable to decrease the catalyst deactivation and our results are consistent with the trends that they reported. *Agrell et al.* [25] reported that zinc promotes and stabilize the copper performance and remove the contribution of sintering in the deactivation of copper catalyst. Carbon deposited on the surface of a catalyst covers the copper sites, therefore, sites available for methanol adsorption during methanol steam reforming reaction decreases. *Agarwa et al.* [21] determined the amount of carbon deposited on catalyst by oxidation in air using a TGA/DTA. They reported that coking content was below 1wt%. Their elemental analysis indicates that this is a light coke hardly evolved with an H/C ratio between 1 and 1.5. These cokes are related to a hydrogen rich atmosphere affecting condensation and cyclization steps of coke formation. Their XPS study revealed that there were two carbon species: graphite carbon (-C-C) and oxidized carbon species (CO₃).

As reported in Table 1 the average crystallite size, calculated by Scherrer's equation from the XRD results, increases as a result of the reaction, however the extent of size enlargement are not so high. Thus, it appears that in our reaction system the main cause of deactivation to be coke formation as the TPO result of this table shows.

CONCLUSIONS

For the first time, the effect of cyclic regeneration of deactivated Cu/ZnO/Al₂O₃ catalysts in steam reforming of methanol is investigated under various conditions. The catalyst significantly deactivate during 1-2 days on stream. Regeneration of the catalyst in diluted O₂ results in dramatic enhancements of the methanol conversion. The hydrogen selectivity also significantly declines during the catalyst deactivation. The regeneration brings back the catalyst activation. The regeneration brings the catalyst hydrogen selectivity back to that of the fresh catalyst, but reduces CO selectivity below the fresh catalyst. Sintering seems not to be the main cause of the deactivation. Small amount of soft cokes are formed on the catalyst too, most of which is burned out at the regeneration temperature. This may contribute to major deactivation of the catalyst. This reason results in dramatically higher activity of the deactivated catalyst after regeneration. Studies of parameters show lower loss of conversion at lower oxygen concentrations. Higher H₂O/Methanol molar ratio in the feed (in the range of 1.1 to 2) shows lower deactivation and loss of conversion.

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