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Methanol steam reforming; Effects of various metal oxides on the properties of a Cu-based catalyst

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Abstract

Ternary Cu/ZnO/metal oxide catalysts are prepared through the co-precipitation method under strict control of parameters like pH, calcination conditions, and precipitation temperature in a systematic manner. The metal oxides applied in this study consist of Al₂O₃, ZrO₂, La₂O₃ and Ce₂O₃. The distinction of this work in comparison with similar research is a comprehensive investigation of the catalytic properties of metal oxides (including conversion, selectivity and stability) which have the potential for use in the methanol steam reforming process. The catalysts are characterized through XRD, SEM and BET. The prepared catalysts are applied in methanol steam reforming in a fixed bed reactor. A TGA analysis performed for all four catalysts determined that the Ce₂O₃ and ZrO₂ metal oxide catalysts showed the best results in terms of stability with a coke formation of 0.7wt% and 0.8wt%, respectively; and maximum surface area is related to Cu/ZnO/Ce₂O₃, which can result in excellent stability and Cu dispersion. Overall, the obtained results indicate that the ZrO₂ metal oxide catalyst is the best candidate to be applied in methanol steam reforming due to its higher activity, selectivity and yield. The hydrogen selectivity and yield of Cu/ZnO/ZrO₂ after 6 hours of experiment were 80.02% and 46.4%, respectively.

1. Introduction

As far as energy sustainability is concerned, depletion of fossil fuel resources is a major international issue. This potential high risk outlook of an “Energy

shortage crises” predicts that the world fossil fuel demand will outstrip its supply [1]. Futurestic studies are full of predictions regarding hydrogen fuel cells as candidates in generating electrical power for hardly accessible (Mobile) systems.

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Since H₂ storage technologies are limited [2] and the necessity of converting liquid fuel into H₂ [3] this issue is of major concern. Conventional hydrogen production methods consume gasoline or use natural gas reforming. Among the different feed stock fuels available, alcohols are very appropriate candidates due to their easy decomposition in presence of water and their generation of a rich hydrogen mixture at relatively low temperatures [4]. Methanol has been commonly studied due to its considerable advantages [5-8], one of which is a high hydrogen to carbon ratio, with low soot formation due to the absence of carbon-carbon bonds, which may otherwise lead to catalyst deactivation [9, 10]. It also exists as liquid at room temperature. Therefore, the required refueling system is compatible with present gasoline distribution infrastructures. Furthermore, it can be extracted from renewable resources and is biodegradable [11]. Methanol is easy to store and transport due to its liquid state at ambient temperatures in comparison to preserving H₂ in cryogenic conditions or under high pressure [12,13].

The three main reactions conventionally contributing to steam reforming of methanol include:

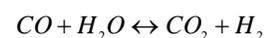
1. Steam Reforming of Methanol (SRM):



2. Methanol Decomposition (MD):



3. Water-Gas Shift (WGS):



The Cu-based catalysts are consumed in hydrogen production through methanol steam reforming [14–20]. Among the Cu-based catalysts, the commercial CuO/ZnO/Al₂O₃ is the most widely consumed. ZnO is added to improve the dispersion and redox characterizations of the copper phases, while support is added to increase the surface area and prevent sintering of the Cu. The amount of consumed Al₂O₃ is usually low because high concentrations have negative effects on the catalytic activity [21]. Due to the negative impacts of Al₂O₃ support on methanol steam reforming catalysts, it is necessary to add another component to the CuO/ZnO/Al₂O₃ catalysts

or simply choose other supports rather than alumina. Compared with the conventional Al₂O₃-supported Cu catalysts, the ZrO₂- or CeO₂-containing catalysts demonstrated increased activities and reduced CO levels in the SRM reaction [22–24]. The promoting effects of ZrO₂ are attributed to Cu dispersion improvement [25] and prevention of CuAl₂O₄ spinel formation [26]. Likewise, consumption of CeO₂, as either a carrier or a promoter, increases the stability of the catalyst and decreases the CO content in the reforming gas [27].

The Cu/ZnO/ZrO₂ catalyst for steam reforming of methanol is assessed by Matsumura [28], where, observations indicate that although the Cu content of a supported catalyst is cut in half, the activity of the catalyst is higher due to a higher Cu dispersion and surface activity.

Most of the previous research consume alumina, ceria and zirconia as the catalyst support in catalytic reforming of methanol, but there exists no comparisons between their performances. In this article, a comprehensive study is performed on catalyst surfaces boosted by alumina, ceria, and zirconia as well as lanthanum oxide and their performances are compared by means of methanol conversion, hydrogen selectivity and catalyst stability.

2. Experimental

2.1. Catalyst preparation

The catalysts are prepared by adopting the co-precipitation method, where, an aqueous solution of Na₂CO₃ (1 M) is added dropwise to an aqueous solution of metal nitrates (1 M) at 60 °C subject to continuous stirring. The volumes of the solutions are adjusted in a manner that the ratio of Cu/ZnO/Metal oxide is 4/5/1 (molar ratio). During precipitation, the pH of the suspension is monitored through a pH meter and the Na₂CO₃ solution is added at a controlled rate in order to maintain the prescribed pH (around 6). After stirring for 90 min, the precipitate is aged for 30 min at room temperature and the resulting precipitate

is then filtered out three times and rinsed for 15 min between each filtering. The precipitate is then dried for 14 h at 110 °C and calcined by air flow for 4 h at gradual temperature rise up to 400 °C.

2.2. Catalyst Characterization

The XRD, SEM, and BET analysis are run to study the structure of the catalysts. The X-ray diffraction (XRD) is performed on a powder diffraction unit, subject to mono-chromatized Cu K α radiation at 300 mA and 40 kV. The diffraction pattern is defined by comparing it with those available in the joint committee of powder diffraction standards (JCPDS) database. Scanning electron microscope (SEM) analysis are run through a JEOL JSM-6340 microscope. BET analysis is run through PHS-1020(PHSCHINA).

2.3. Catalytic performance test

To evaluate the performance of the catalysts, the runs are performed by applying a conventional fixed-bed reactor (S.S.304, 5mm internal diameter). The catalyst is first pelleted and placed in the reactor and heated up to 200 °C subject to N₂ flow for 15 min. The catalyst bed is then reduced subject to 50 ml min⁻¹ H₂ flow at 300 °C for 45 min. Following this a saturated solution of methanol and water (steam/methanol=1.5 molar ratio) is injected into the reactor at weight hourly space velocity (WHSV) of 40 h⁻¹ through a vaporizer heated up to 250°C. The catalytic performance

is measured at 30-minute intervals up to 6 hours for every four units of produced catalysts. The test set-up and the related procedures are shown in Fig.1. The produced gas from the performance test is analyzed by on-line gas chromatographs (GC). A GC which is composed of packed molecular sieves 5 °A column (3m×3mm i.d.), Ar carrier gas and TCD detector to analyze H₂ and CO. Another plot-Q column (3m×3mm i.d.), He carrier gas and TCD detector is necessary to analyze CO₂. The unreacted CH₃OH, and H₂O are trapped and measured in order to calculate conversion and omitting the negative effect of condensation on selectivity calculations.

Definition of mentioned parameters are as follows:

$$\text{Conversion} = \frac{(Feed_{in} - Feed_{out})_{mol}}{(Feed_{in})_{mol}} \times 100 \quad (1)$$

$$\text{Selectivity of product}(i) = \frac{\text{moles of product}(i)}{\text{moles of all products}} \times 100 \quad (2)$$

2.4. Catalyst stability test

Thermogravimetric Analysis (TGA) is performed with a catalyst weight of 5 mg at a gradual heating rate of 10 °C/min up to 800 °C in an atmosphere of 10 vol% Ar (100 ml.h⁻¹). Weight losses of coke depletion are compared to assess the stability of the prepared catalysts.

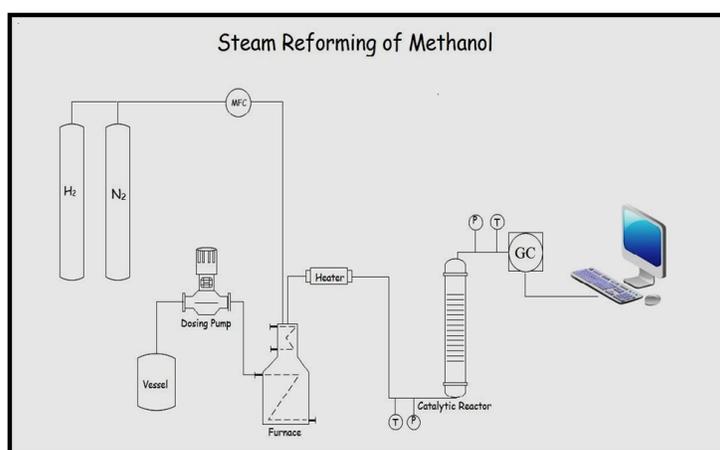


Fig. 1. Schematic of the performance test set-up.

3. Results and discussion

3.1. Characterization of the catalysts

The XRD patterns of the prepared catalysts are shown in Fig. 2. As observed, the catalysts are well prepared. The average Cu crystallite size of each catalyst is calculated through the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

where λ is the wavelength of the X-ray, θ is the

diffracting angle, constant k is equal to 0.9 and β is the full width of diffraction peak at half maximum intensity (FWHM). Results showed an average Cu crystallite size of 17.73 nm, 12.96 nm, 6.60 nm and 6.14 nm for ZrO_2 , Ce_2O_3 , Al_2O_3 and La_2O_3 catalysts, respectively.

The SEM images (Fig. 3) show the good sphericity and regular morphology of the crystals, moreover the particle size obtained from SEM for the four prepared catalysts is about 40 nm.

Results of BET analysis (Table 1) indicate that the surface area of ZrO_2 and Ce_2O_3 catalysts are

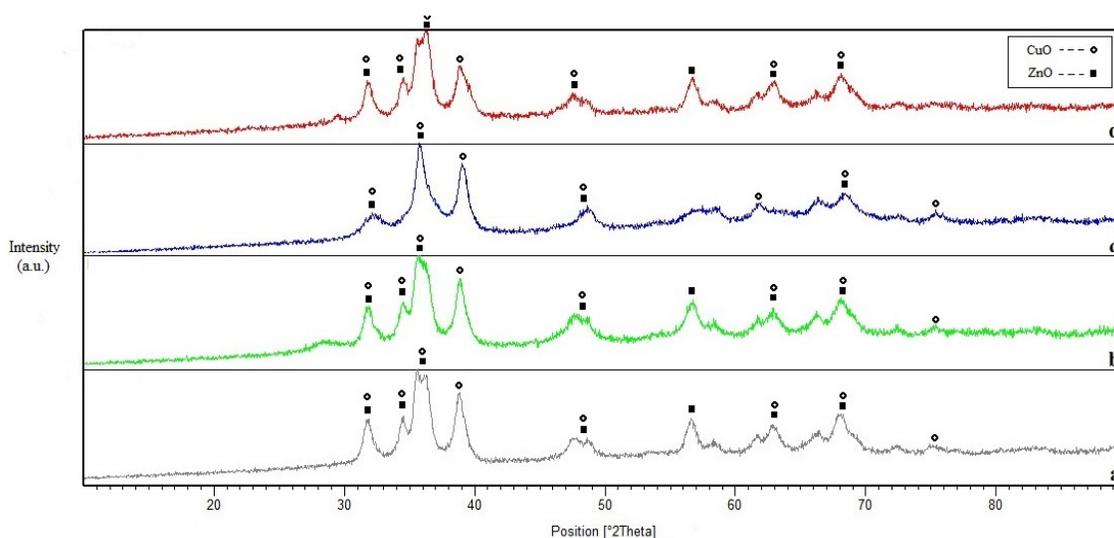


Fig. 2. XRD patterns of the prepared Cu/ZnO catalysts: a) Al_2O_3 , b) La_2O_3 , c) Ce_2O_3 , d) ZrO_2 .

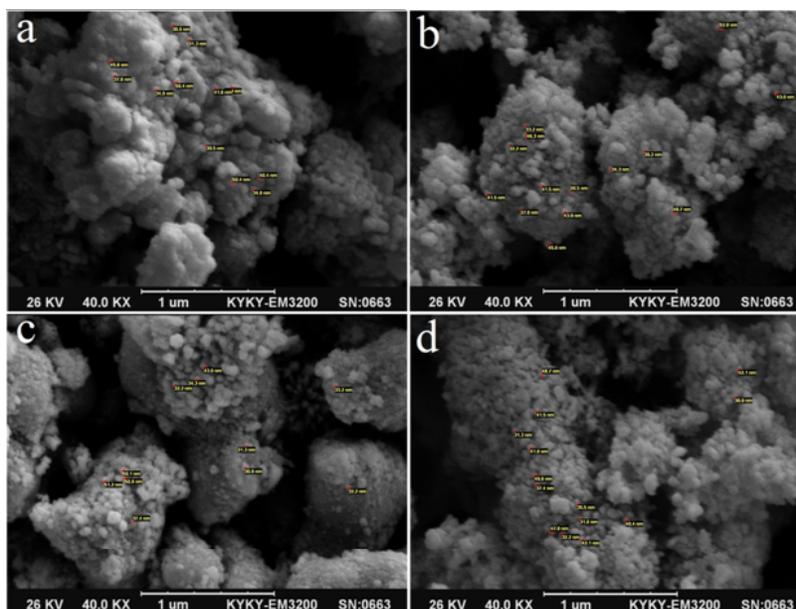


Fig. 3. SEM images of the prepared Cu/ZnO catalysts: a) Al_2O_3 , b) La_2O_3 , c) Ce_2O_3 , d) ZrO_2 .

significantly higher than the other two catalysts, which in turn enhance the dispersion of Cu and improve the catalytic performance.

3.2. Effects of the catalyst metal oxide on activity, selectivity and yield

According to Fig. 4 the maximum conversion is of the Ce_2O_3 and ZrO_2 metal oxide catalysts and ZrO_2 and Al_2O_3 show the maximum amount of hydrogen

selectivity among the other catalysts, (Fig. 5). As the catalyst yield is the product of the Multiplication of selectivity and conversion, the best yield in all time periods is for $Cu/ZnO/ZrO_2$, as observed in Fig. 5, it is clear that the conversion curves show an excellent agreements with the results of the BET. Regarding the undesired effect of carbon monoxide formation, CO selectivity in all samples is below 2% which is expected due to the absence of CO in the main reaction of methanol steam reforming (Fig. 6).

Table 1. Surface areas of prepared catalysts

$Cu/ZnO/ZrO_2$	$Cu/ZnO/Ce_2O_3$	$Cu/ZnO/La_2O_3$	$Cu/ZnO/Al_2O_3$	Catalyst
58.280	64.696	42.936	38.397	Surface Area (m ² /g)

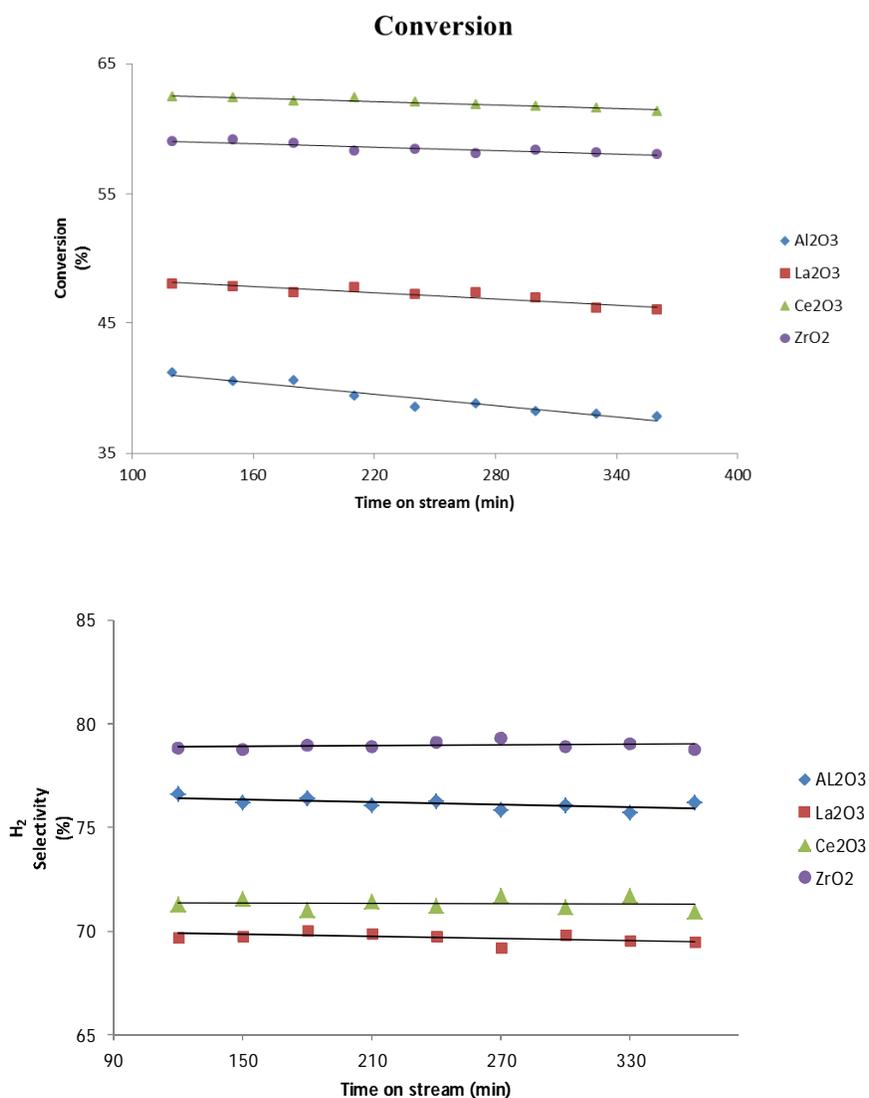


Fig. 5. H_2 selectivity of the catalysts during the six hours of experiment.

Despite the higher performance of ZrO_2 and Ce_2O_3 in comparison with that of the industrial Al_2O_3 metal oxide catalyst, is not rational to apply $Cu/ZnO/Al_2O_3$ in the SRM process due to its lower amount of activity and yield and higher rate of deactivation. It is notable that the $Cu/ZnO/Al_2O_3$ prepared catalyst exhibited almost the same performance as its industrial counterpart.

3.3. Effects of metal oxide on stability

The experiments run in a 6 h period illustrate that the conversion drop of ZrO_2 metal oxide catalyst is less than the other prepared catalyst; moreover, the hydrogen selectivity of all four catalysts has minor

variation. These two concepts reveal the proper consistency of the prepared catalysts in both activity and selectivity terms. Accordingly, in the case of selectivity, H_2 selectivity of the prepared catalysts are in the range of 69 to 80% (Fig. 5).

In addition to the importance of application consistency, the stability of the catalyst in continuous periods of time contributes greatly to catalyst utilization. The stability is assessed through TGA analysis (Fig. 7), indicating that the Ce_2O_3 metal oxide catalyst with a coke formation of 0.7 wt%, has the best stability after 6 hour of performance; however, the coke formation of $Cu/ZnO/ZrO_2$ is close to that of Ce_2O_3 at about 0.8wt%. The coke content of Al_2O_3 and La_2O_3 support catalysts after 6 hour of

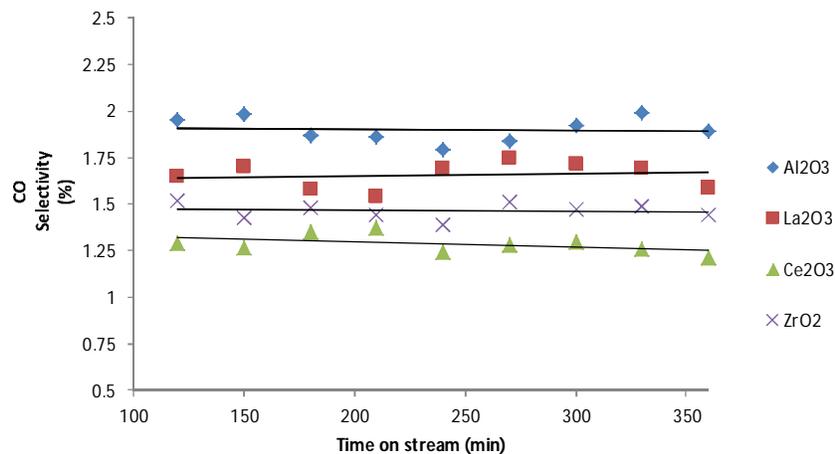


Fig. 6. CO selectivity of the catalysts during the six hours of experiment.

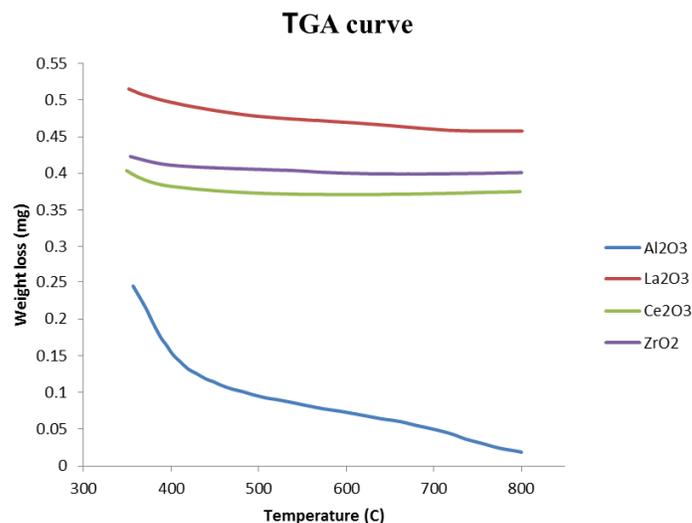


Fig. 7. Thermogravimetric analysis of the prepared catalysts.

experiment are 8 wt% and 2.2 wt%, respectively. It can be concluded that Ce_2O_3 and ZrO_2 metal oxide catalysts exhibit the best tolerance against the deactivation process.

4. Conclusions

According to the extensive studies run on transition metal oxides for choosing in this process, results indicate that the ZrO_2 metal oxide catalyst exhibits the best performance as to yield and hydrogen selectivity among other Cu based methanol reforming catalysts. This fact may be due to large Cu crystallite size, appropriate surface area and ZrO_2 's ability to improve Cu reducibility by developing major reaction intermediates on its surface.

The large size of Cu crystals in Ce_2O_3 and ZrO_2 metal oxide catalysts can interpret the high performance of these catalysts due to the fact that growth in Cu crystallites affect the structure of the catalysts and create new active sites; moreover, an increase in Cu crystallinity leads to an increase in the delocalization of its electron and hole pairs, which in turn can lead to active size incremenation.

The conversion observations interpreted by BET results indicate that greater catalyst porosity improves the conversion of Cu-ZnO-Metal oxide. As to stability, Ce_2O_3 and ZrO_2 metal oxide catalysts have the maximum durability among the four prepared catalysts, which is predictable by their BET results and better dispersion regarding Al_2O_3 and La_2O_3 metal oxide catalysts.

Nomenclature

D Mean size of crystallites (nm)
 k Dimensionless crystallite shape factor

Greek Letters

β Full width of diffraction peak at half maximum intensity (rad)

λ Wave length of the X-ray (nm)
 θ diffracting angle (deg)

Abbreviations

BET Brunauer– Emmett– Teller
 FWHM Full width at half maximum
 JCPDS Joint committee of powder diffraction standards
 SEM Scanning electron microscope
 SRM Steam reforming of Methanol
 TGA Thermogravimetric analysis
 WHSV Weight hourly space velocity
 XRD X-ray diffraction

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